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(54) 【発明の名称】 有機電界発光素子

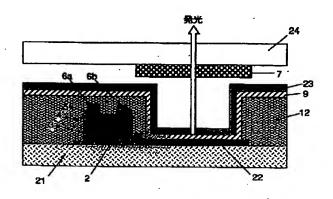
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(修正有)

【課題】 優れた表示能力を有する有機電界発光素子を、歩留まり良く低コストで製造する。

【解決手段】 アクティブ・マトリクス回路および有機 電界発光セルを形成した絶縁性基板と、発光変換層を設 けた透明支持基板を対向して設けたことを特徴とする有 機電界発光素子。



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【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は有機電界発光案子に 関するものであり、詳しくは、有機化合物から成る発光 層に電界をかけて光を放出する薄膜型デバイスに関する ものである。

[0002]

【従来の技術】従来、薄膜型の電界発光(EL)案子としては、無機材料のII-VI族化合物半導体であるZnS、CaS、SrS等に、発光中心であるMnや希土類 10元素(Eu、Ce、Tb、Sm等)をドープしたものが一般的であるが、上記の無機材料から作製したEL案子は、

- 1) 交流駆動が必要(50~1000Hz)、
- 2) 駆動電圧が高い (~200V)、
- 3) フルカラー化が困難(特に青色)、
- 4) 周辺駆動回路のコストが高い、

という問題点を有している。

【0003】しかし、近年、上記問題点の改良のため、有機薄膜を用いたEL素子の開発が行われるようになっ 20 た。特に、発光効率を高めるため、電極からのキャリアー注入の効率向上を目的として電極の種類の最適化を行い、芳香族ジアミンから成る正孔輸送層と8ーヒドロキシキノリンのアルミニウム錯体から成る発光層とを設けた有機電界発光素子の開発(Appl. Phys. Lett.,51巻,913頁,1987年)により、従来のアントラセン等の単結晶を用いたEL素子と比較して発光効率の大幅な改善がなされ、実用特性に近づいている。

【0004】上記の様な低分子材料を用いた電界発光素 30 子の他にも、発光層の材料として、ポリ(pーフェニレ ンピニレン) (Nature, 347巻, 539頁, 1 990年他)、ポリ〔2-メトキシ-5-(2-エチル ヘキシルオキシ) -1, 4-フェニレンビニレン] (A ppl. Phys. Lett., 58巻, 1982頁, 1991年他)、ポリ(3-アルキルチオフェン)(J pn. J. Appl. Phys. 30巻, L1938 頁、1991年他)等の高分子材料を用いた電界発光素 子の開発や、ポリビニルカルバゾール等の高分子に低分 子の発光材料と電子移動材料を混合した素子(応用物 理, 61巻, 1044頁, 1992年) の開発も行われ ている。また、例えば、8-ヒドロキシキノリンのアル ミニウム錯体をホスト材料として、クマリン等のレーザ 用蛍光色素をドープすること (J. Appl. Phy s. 65巻, 3610頁, 1989年) 等も行われてい る。

[0005]

【発明が解決しようとする課題】上記の様な有機電界発 光素子をディスプレイパネルとして用いるためには、一 般にマトリクスアドレス方式(特開平2-66873号 50 公報;電気通信学会技術研究報告,OME 8 9 - 4 6,37,1989年)が採用されるが、画案数の増加にともない、輝度がデューティ比の減少とともに減少する(電気通信学会技術研究報告,OME 8 8 - 4 7,35,1988年)ことや、クロストークが起きることが実用上大きな問題となっている。さらには、走査線の数の増加とともに、ダイナミック駆動時には瞬間的に高輝度発光させる必要が生じ、結果として、駆動電圧の増加と電力変換効率の低下を招く。

【0006】この単純マトリクス駆動方式の問題を解決するために、有機電界発光素子をアクティブ・マトリクス回路で駆動することが考えられる(特開平6-325869号公報;特開平7-122362号公報;特開平8-54836号公報;特開平8-330600号公報)。しかしながら、フルカラー化に関しては大きな問題点がある。

【0007】これまでに、フルカラー化の方式についてはいくつかの提案がなされている:

- 1) 有機発光素子を各発光色 (RGB) に応じてパター ニングして平面配置する方式 (Appl. Phys. L ett., 69巻, 3117頁, 1996年)、
- 2) 微小共振器構造を用いる方式 (Jpn. J. App
 l. Phys. 34巻, L1234頁, 1995年)、
- 3) 白色発光素子とカラーフィルタを組み合わせる方式 (特開平7-142169号公報)、
- 4) 青色発光素子と蛍光変換層を組み合わせる方式 (特 開平3-152897号公報)、
- 5) RGB発光層を積層する方式 (フランス特許第2, 728,082号)。

【0008】1)の方式は、プロセス上有機層に適用す ることが困難であり、2)の方式は高価なハーフミラー を必要とすること視野角により波長がずれるという問題 を有している。3)の方式では、積層型にすることで、 RGB各発光層の配線を垂直方向に絶縁をとる必要が生 じ、配線が非常に複雑になる。3)及び4)の方式で は、有機層はベタに形成できることから、両方式が現在 のところフルカラーパネルに採用可能な方式である。 【0009】フルカラーパネルは、QVGA仕様(32 0×240ドット)以上のレベルの画案数が想定される ので、基本的にはアクティブ・マトリクス駆動型にな る。前述の3)及び4)の方式をアクティブ・マトリク ス回路と両立させる方法が必要である。これまでに、開 示されている方法(特開平6-325869号公報)で は、各画案の有機電界発光セルがアクティブ・マトリク ス駆動回路の案子(TFT)と同一基板上に形成され、 かつ、発光変換層(カラーフィルタ層または蛍光変換 層) が基板の外側か素子側に形成されている。図1は従 来の一般的な有機電界発光索子の構造例を模式的に示す

断面図であり、1は透明基板、2~6はTFT、7は発

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ウム、ユーロピウム、ガドリニウム、ハフニウム、インジウム、ランタン、マグネシウム、マンガン、ネオジウム、スカンジウム、サマリウム、イットリウム、亜鉛、ジルコニウム等の金属や、これらの金属と先に挙げた仕事関数が4.6 e V以上の値を有する金属との合金組成物も使用される。また、LaB6等の化合物材料もこの目的で可能である。この低仕事関数材料層の膜厚は、透明性の要請から、1~100nm、好ましくは0.5~50nm程度である。この低仕事関数材料層の上に前述のITO、ZnO等の透明導電層が、膜厚5~1000nm、好ましくは10~500nm程度で積層される。各下部電極に対してスイッチング及びメモリー機能を有するアクティブ駆動回路が基板上に形成されているので、上部電極については表示面積全体にわたってベタの成膜で構わない。

【0017】上記の低仕事関数材料層の代わりに、トンネル障壁効果により陰極から発光層への電子注入を容易にする界面層を用いてもよい。この目的に使用される材料としては、LiFやNaF等のアルカリ金属フッ化物、MgF2、CaF2等のアルカリ土類金属のフッ化物、Li2〇等のアルカリ金属酸化物、MgO、Ba.〇等のアルカリ土類金属の酸化物から成り、これらの材料絶縁性であることから、膜厚としては0.2~10 nmの範囲が好ましい。

【0018】下部電極、上部電極の形成方法は、抵抗加熱方式または電子ビーム方式による真空蒸着法、スパッター法、ECRスパッタ法、イオンビームスパッタ法等が用いられる。次に、有機発光層9の構造について説明する。発光材料を単層で形成することも可能であるが、発光効率を高くするためには、正孔輸送層と電子輸送層を少なくとも含む構造が望ましい。図5は本発明に用いられる一般的な有機電界発光セルの構造例を模式的に示す断面図であり、21は基板、22は下部電極(陽極)、41は正孔輸送層、42は電子輸送層、23は上部電極(陰極)を各々表わす。

【0019】正孔輸送層41の材料に要求される条件としては、下部電極22からの正孔注入効率が高く、かつ、注入された正孔を効率よく輸送することができる材料であることが必要である。そのためには、イオン化ポテンシャルが小さく、可視光の光に対して透明性が高く、しかも正孔移動度が大きく、さらに安定性に優れ、トラップとなる不純物が製造時や使用時に発生しにくいことが要求される。上記の一般的要求以外に、車載表示用の応用を考えた場合、案子にはさらに耐熱性が要求される。従って、Tgとして70℃以上の値を有する材料が望ましい。

【0020】このような正孔輸送材料としては、例えば、1,1-ビス(4-ジ-p-トリルアミノフェニル)シクロヘキサン等の3級芳香族アミンユニットを連結した芳香族ジアミン化合物(特開昭59-19439 50

3号公報)、4,4'-ピス[N-(1-ナフチル)-N-フェニルアミノ] ピフェニルで代表される2個以上 の3級アミンを含み2個以上の縮合芳香族環が窒素原子 に置換した芳香族アミン (特開平5-234681号公 報)、トリフェニルベンゼンの誘導体でスターバースト 構造を有する芳香族トリアミン(米国特許第4, 92 3, 774号)、N, N'ージフェニルーN, N'ービ ス (3-メチルフェニル) ピフェニルー4、4′-ジア ミン等の芳香族ジアミン(米国特許第4, 764, 62 5号)、 α , α' , α' ーテトラメチルー α , α' ービス (4ージーpートリルアミノフェニル) ーpーキ シレン(特開平3-269084号公報)、分子全体と して立体的に非対称なトリフェニルアミン誘導体(特開 平4-129271号公報)、ピレニル基に芳香族ジア ミノ基が複数個置換した化合物(特開平4-17539 5号公報)、エチレン基で3級芳香族アミンユニットを 連結した芳香族ジアミン(特開平4-264189号公 報)、スチリル構造を有する芳香族ジアミン(特開平4 -290851号公報)、チオフェン基で芳香族3級ア ミンユニットを連結したもの(特開平4-304466 号公報)、スターバースト型芳香族トリアミン (特開平 4-308688号公報)、ベンジルフェニル化合物 (特開平4-364153号公報)、フルオレン基で3 級アミンを連結したもの(特開平5-25473号公 報)、トリアミン化合物(特開平5-239455号公 報)、ビスジピリジルアミノビフェニル(特開平5-3 20634号公報)、N, N, N-トリフェニルアミン 誘導体(特開平6-1972号公報)、フェノキサジン 構造を有する芳香族ジアミン(特開平7-138562 **号公報)、ジアミノフェニルフェナントリジン誘導体** (特開平7-252474号公報)、ヒドラゾン化合物 (特開平2-311591号公報)、シラザン化合物 (米国特許第4, 950, 950号公報)、シラナミン 誘導体(特開平6-49079号公報)、ホスファミン 誘導体(特開平6-25659号公報)、キナクリドン 化合物等が挙げられる。これらの化合物は、単独で用い てもよいし、必要に応じて、各々、混合して用いてもよ い。

【0021】上記の化合物以外に、正孔輸送層41の材料として、ポリビニルカルバゾールやポリシラン(Appl. Phys. Lett.,59巻,2760頁,1991年)、ポリフォスファゼン(特開平5-310949号公報)、ポリビニルトリフェニルアミン(特開平7-53953号公報)、トリフェニルアミン骨格を有する高分子(特開平4-133065号公報)、トリフェニルアミン単位をメチレン基等で連結した高分子(Synthetic Metals,55-57巻,4163頁,1993年)、芳香族アミンを含有するポリメタクリレート(J. Polym. Sci., Polym. C

トラフェニルブタジエンなどの芳香族化合物 (特開昭5 7-51781号公報)、8-ヒドロキシキノリンのア ルミニウム錯体などの金属錯体(特開昭59-1943 93号公報)、10-ヒドロキシベンゾ [h] キノリン の金属錯体(特開平6-322362号公報)、混合配 位子アルミニウムキレート錯体(特開平5-19837 7号公報、特開平5-198378号公報、特開平5-214332号公報、特開平6-172751号公報シ クロペンタジエン誘導体(特開平2-289675号公 報)、ペリノン誘導体(特開平2-289676号公 報)、オキサジアソール誘導体(特開平2-21679 1号公報)、ビススチリルベンゼン誘導体(特開平1-245087号公報、同2-222484号公報)、ペ リレン誘導体(特開平2-189890号公報、同3-791号公報)、クマリン化合物(特開平2-1916 94号公報、同3-792号公報)、希土類錯体(特開 平1-256584号公報)、ジスチリルピラジン誘導 体 (特開平2-252793号公報)、p-フェニレン 化合物(特開平3-33183号公報)、チアジアソロ ピリジン誘導体(特開平3-37292号公報)、ピロ 20 ロピリジン誘導体(特開平3-37293号公報)、ナ フチリジン誘導体(特開平3-203982号公報)、 シロール誘導体(日本化学会第70春季年会, 2D1 02及び2D1 03, 1996年) などが挙げられ る。

【0029】電子輸送層42の膜厚は、通常、10~200nm、好ましくは30~100nmである。電子輸送層も正孔輸送層と同様の方法で形成することができるが、通常は真空蒸着法が用いられる。案子の発光効率を向上させるとともに発光色を変える目的で、例えば、8一ヒドロキシキノリンのアルミニウム錯体をホスト材料として、クマリン等のレーザ用蛍光色素をドープすること(J. Appl. Phys., 65巻, 3610頁, 1989年)等が行われている。この方法の利点は、

- 1) 高効率の蛍光色素により発光効率が向上、
- 2) 蛍光色素の選択により発光波長が可変、
- 3) 濃度消光を起こす蛍光色素も使用可能、
- 4) 薄膜性のわるい蛍光色素も使用可能、等が挙げられる。

【0030】案子の駆動寿命を改善する目的において も、前記電子輸送材料をホスト材料として、蛍光色素を ドープすることは有効である。例えば、8-ヒドロキシ キノリンのアルミニウム錯体などの金属錯体をホスト材 料として、ルプレンに代表されるナフタセン誘導体(特 開平4-335087号公報)、キナクリドン誘導体

(特開平5-70773号公報)、ペリレン等の縮合多環芳香族環(特開平5-198377号公報)を、ホスト材料に対して0.1~10重量%ドープすることにより、案子の発光特性、特に駆動安定性を大きく向上させることができる。

【0031】ホスト材料としては、例えば、電子輸送層42がその役割を果たす場合、前述の電子輸送性化合物が挙げられ、正孔輸送層41がホスト材料としての役割を果たす場合、前述の芳香族アミン化合物やヒドラゾン化合物が挙げられる。上記ドーパントが正孔輸送層および/または電子輸送層中にドープされる場合、各層の膜厚方向において均一にドープされるが、膜厚方向において洩度分布があっても構わない。例えば、正孔輸送層との界面近傍にのみドープしたり、逆に、陰極界面近傍にドープしてもよい。

【0032】本発明においては、フルカラー発光を達成するために、以下の2つの方法が考えられる。一つは、素子を白色発光させ、その白色光を、発光変換層としてカラフィルターを用いて青、緑、赤の3色に分解する方法である。もう一つの方法としては、素子を青色発光させて、その青色光を、発光変換層として蛍光変換層を用いることにより、青はそのままの色で取り出し、緑と赤については緑色蛍光材料と赤色蛍光材料により色変換を行うことにより、青、緑、赤の3色を得る。従って、有機発光層としては白色発光または青色発光が可能な層構成とする必要がある。この目的のために、例えば、電子輸送層に発光機能をもたせて、以下の層構成とすることができる。

【0033】白色発光の場合には、図7に示すように、例えば、電子輸送層42を3つの領域42a,42b,42cに分けて、正孔輸送層41に接する方から青色発光層42a、緑色発光層42b、赤色発光層42cとすれば、各層からの発光が重ね合わさって白色発光を得ることができる。白色の色バランスを取るためには、青から赤の各発光層の膜厚を調整することで容易にできる。各色の発光層に用いられる材料としては、既述した電子輸送層に用いられるホスト材料、さらには、ドープ色素と組み合わせて使用することができる。

【0034】青色発光の場合には、既に挙げた電子輸送 層材料のなかで、青色蛍光を示すホスト材料と、必要に 応じて、青色蛍光色素をドープした電子輸送層を形成す ることで、図5および図6に示した構造により、青色発 光を得ることができる。有機電界発光素子の発光効率を さらに向上させる方法として、電子輸送層42の上にさ らに電子注入層43を積層することもできる(図8参 照)。この電子注入層43に用いられる化合物には、陰 極からの電子注入が容易で、電子の輸送能力がさらに大 きいことが要求される。この様な電子輸送材料として は、既に電子輸送層材料として挙げた8-ヒドロキシキ ノリンのアルミ錯体、オキサジアゾール誘導体(App l. Phys. Lett., 55巻, 1489頁, 19 89年他) やそれらをポリメタクリル酸メチル (PMM A) 等の樹脂に分散した系 (Appl. Phys. Le tt.,61巻,2793頁,1992年)、フェナン トロリン誘導体(特開平5-331459号公報)、2

ットエッチング技術により下部電極(陽極) 22及びの ゲート電極のパターニングを行った。この下部電極(陽 極)の仕事関数を、理研計器製表面分析装置(AC-1)で測定したところ4.8eVであった。

【0045】(b)ゲート絶縁膜、半導体層、オーミックコンタクト層成膜工程

工程 (a) で作製した基板を、プラズマCVD装置にセットし、以下の表-1に示す条件で各層 3 b, 4 b, 5 b を連続成膜した。

[0046]

【表1】

_	_
	1

成膜条件	1. SiNx 層	2. i層a-Si	3.n ⁺ 應a-SI	
<ガス流量>	-			
SiH4	10	20	10	
NH3	100	_	-	
Ht2		20	_	
PH3/H2 (0.1%)			100	
基板温度 [で]	300	280	280	
成誕圧力 [Torr]	0.25	0.15	0.33	
電力密度 [W/cm²]	0.14	0.08	0.08	
膜厚 [nm]	300	100 .	50	

20

【0047】(c)a-Siパターニング工程 上記のプラズマCVD装置から基板を取り出して、通常 のフォトリソグラフィー技術とSF6 ガスを用いたプラ ズマエッチングによりa-Siのパターニングを行っ た。

(d) ソース及びドレイン電極形成工程 通常のフォトリソグラフィー技術と電子ピーム蒸着により、50nmのCr層と100nmのAl層とを順次積 層したドレイン及びソース電極を形成した。

【0048】(e)n・aーSi層エッチオフ工程 通常のフォトリソグラフィー技術とSF6 ガスを用いた プラズマエッチングにより、ソース及びドレイン電極を マスクとしてn・aーSiの層のエッチングを行い、チャンネルを形成した。上記工程(a)~工程(e)で作 製した有機電界発光パネルのaーSiTFTの特性を評 価したところ、移動度(μFE)は0.5cm²/V・sec、しきい値は3Vであった。

【0049】(f) アクティブ・マトリクス回路保護用の絶縁膜形成工程

アルカリ現像型透明耐熱レジスト材料(新日鉄化学 (株)製;V-259PA)を用いて通常のフォトリソグラフィー技術により膜厚1.3μmの絶縁層を形成した。

(g) 有機電界発光層成膜工程(白色発光セル) 工程(f) までで出来上がった駆動回路基板を、イソプロピルアルコールで超音波洗浄、純水で水洗、乾燥窒素で乾燥、UV/オゾン洗浄を行った後、蒸着部分を限定する密着マスクをつけて真空蒸着装置内に設置し、装置 内の真空度が2×10⁻⁶ Torr以下になるまで油拡散 ポンプを用いて排気した。

【0050】以下、図7に示す構造の白色発光機能を有する有機電界発光素子部分を作製した。上記真空装置内に配置されたモリブデンボートに入れた以下に示す銅フタロシアニン(H1)(結晶形は β 型)を加熱して蒸着を行った。真空度 2×10^{-6} Torr(約2.7×10 $^{-4}$ Pa)、蒸着速度0.3 nm/秒で蒸着を行ない、膜厚20 nmの陽極バッファ層40を得た。

[0051]

【化1】

【0052】次に、前記装置内に配置されたセラミックるつぼに入れた、以下に示す、4,4'-ビス[N-(1-ナフチル)-N-フェニルアミノ] ピフェニル(H2) をるつぼの周

[0053]

【化2】

mのシリカビーズを分散させることにより、有機発光セル基板とカラーフィルタ基板との距離を $5~\mu$ mと設定した。カラーフィルタは通常知られている方法に従って、カラーレジストを用いて形成し、その上に透明平滑化層を設け、全膜厚は $3~\mu$ mとした。

【0062】上記の工程で完成した、有機電界発光案子を駆動させたところ、各カラーフィルタ層で変換された赤、緑、青の発光が確認できた。また、青、緑、赤の各サブピクセルの発光輝度を階調制御することにより、フルカラー画像を達成できた。

実施例2 (方法B)

方法Bに従って、以下に示すプロセスで素子を作製した。 TFT素子の設計は、実施例1と同じである。以下 に各製作工程について、図8に従って説明する。

(a') 下部電極及びゲート電極形成工程

無アルカリガラス(コーニング社製 7 0 5 9)基板上に、A 1 を膜厚 2 0 0 n m、さらに C r を膜厚 5 0 n mでスパッタリング法で形成したものを、通常のフォトリソグラフィー技術とウェットエッチング技術により下部電極(陰極) 2 2 及びゲート電極のパターニングを行った。

【0063】工程(b)~工程(f)は実施例1と同様 にして行う。

(g') 有機電界発光層成膜工程(青色発光セル)引き続いて、下部電極(陰極)の低仕事関数層を、以下の方法で形成した。工程(f)までので出来上がった駆動回路基板を、イソプロピルアルコールで超音波洗浄、純水で水洗、乾燥窒素で乾燥、UV/オゾン洗浄を行った後、蒸着領域及び電極取り出し部を規定するシャドーマスクを素子に密着させて、真空蒸着装置内に設置して30有機層と同様にして装置内の真空度が2×10-6 Torr(約2.7×10-1 Pa)以下になるまで排気した。下部電極の低仕事関数層として、マグネシウムと銀の合金電極を2元同時蒸着法によって膜厚50nmとなるように蒸着した。このマグネシウム合金の仕事関数は、3.6 e Vであった。

【0064】以下、図8に示す構造の白色発光機能を有する有機電界発光素子部分を作製した。実施例1の作製工程と同様にして、銅フタロシアニン(H1)から成る膜厚20nmの陽極バッファ層40と、4,4′ービス 40 [Nー(1ーナフチル)ーNーフェニルアミノ] ビフェニル(H2) から成る膜厚60nmの正孔輸送層41を形成した。次に、青色発光機能を有する電子輸送層42のホスト材料として、以下の構造式に示す2ーメチルー8ーヒドロキシキノリンのアルミニウム2角錯体(E1)と、

[0065]

【化5】

【0066】ドープ色素として以下の構造式に示すペリレン(D2)を、各々、別々のるつぼ

[0067]

【0068】を用いて2元蒸着を行った。この時のアルミニウム2核錯体のるつぼ温度は300~320℃の範囲で、ペリレンのるつぼ温度は110~120℃の範囲で制御し、蒸着時の真空度は1.8×10-6 Torr (約2.4×10-4 Pa)、蒸着速度は0.2~0.3 nm/秒で、膜厚45nmの青色発光層を正孔輸送層41の上に積層した。

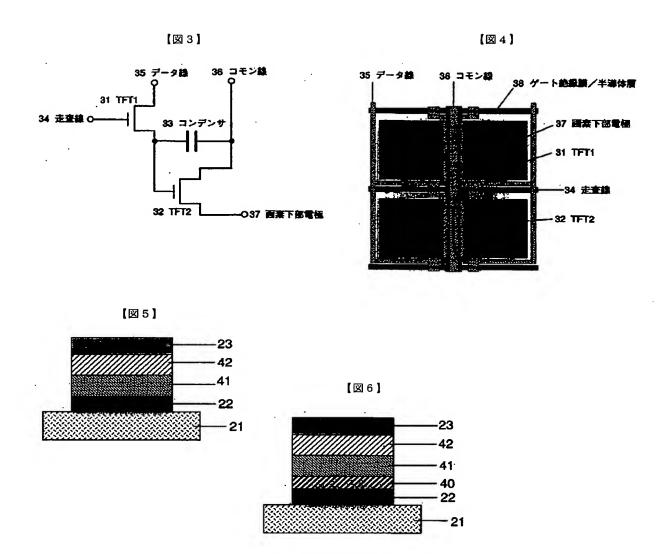
【0069】最後に、電子注入層としてアルミニウムの8-ヒドロキシキノリン錯体(E2)を用いた。この時のアルミニウムの8-ヒドロキシキノリン錯体のるつぼ温度は270~280℃の範囲で制御し、蒸着時の真空度は1.3×10-6 Torr(約1.7×10-4 Pa)、蒸着速度は0.2~0.3nm/秒で、膜厚30nmの電子注入層を電子輸送層の上に積層した。上記の陽極バッファ層40、正孔輸送層41、電子輸送層42及び電子注入層43を真空蒸着する時の基板温度は室温に保持した。

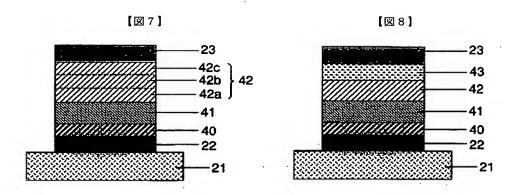
【0070】(h')上部電極形成工程

続いて、上部電極(陽極)として、ITO膜を150nmの膜厚で形成した。スパッタは通常のRFマグネトロンスパッタ法により、素子は加熱せずに行った。ITOのスパッタ条件としては、アルゴンー酸素の混合ガス

(酸素濃度 0. 1%)、圧力 3×10⁻³ Torr(約0.4Pa)、電力密度 0.1W/cm²、ターゲットと基板間距離はプラズマダメージを防ぐために 10cmとした。この陽極の仕事関数は 4.7eVであった。

【0071】続いて、方法Aと同様にして、保護膜形成工程(i)を経た後、発光変換層として蛍光変換層を用いた他は実施例1と同様にして封止工程(j)を行い、全行程を完了させた。蛍光変換層としては青色発光はそのまま用いるので必要なく、緑色蛍光変換層に関してはクマリン6をPMMAに3重量%分散させたものを、赤色蛍光変換層としてはクマリン6を1重量%、フェノキ







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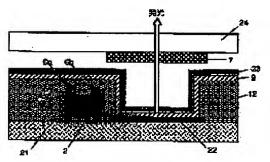
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(54) ORGANIC ELECTROLUMINESCNET ELEMENT

(57) Abstract:

PROBLEM TO BE SOLVED: To improve a display state and raise the yield of a panel for reducing production cost by constituting such that a transparent support body having a luminous conversion layer is provided, so as to be faced to an insulation substrate having an organic electroluminescent cell made of an organic luminous layer or the like clamped with a cathode and an anode, and an active matrix circuit element for driving the cell, respectively at an upper level.

SOLUTION: TFTs 2 to 6, and an organic electroluminescent cell clamped with a lower electrode 22 and an upper electrode 23, and formed out of an organic luminous layer 9 for forming each pixel are arranged on the insulation substrate 21 made of a glass panel, silicon wafer or the like. Furthermore, the upper electrode 23 formed so as to have transmissivity in a visible ray zone and used as a cathode is preferably a laminate of a low work function material layer, such as Mg and Al coming in contact with the organic luminous layer 9 and giving a work function equal to or below 4 eV, and a transparent conductive layer such as ITO and ZnO, thereby improving electron injection efficiency. Also, a transparent support body 24 with a fluorescent conversion layer, containing a fluorescent pigment or a color filter luminous conversion layer 7, and the insulation substrate 21 are kept at the prescribed gap from each other via a spacer.



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[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

[Claim(s)]

[Claim 1] The organic electroluminescence devices characterized by to prepare the luminescence conversion layer which are the organic electroluminescence cel which was pinched by an anode plate and cathode, and which consists of an organic luminous layer at least, and the organic electroluminescence devices which prepared the active-matrix circuit which drives an organic electroluminescence cel on said insulating substrate, counters with said insulating substrate, is made to arrange a transparence base material on an insulating substrate, and changes luminescence from an organic electroluminescence cel on a transparence base material.

[Claim 2] Organic electroluminescence devices according to claim 1 characterized by establishing said anode plate in the insulating substrate side of an organic electroluminescence cel, establishing said cathode in the transparence base material side of an organic electroluminescence cel, and cathode having 60% or more of permeability in a 400-800nm light field.

[Claim 3] Organic electroluminescence devices according to claim 2 which the laminating of the layer and transparence conductive layer to which said cathode changes from a low work function ingredient 4.0eV or less is carried out, and are characterized by the low work function ingredient layer touching the organic luminous layer. [Claim 4] Organic electroluminescence devices according to claim 3 to which thickness of said low work function ingredient layer is characterized by being in the range of 1–100nm.

[Claim 5] Organic electroluminescence devices given in claim 3 to which said low work function ingredient layer is characterized by being chosen out of a Magnesium alloy and an aluminium alloy thru/or any 1 term of 4. [Claim 6] Organic electroluminescence devices according to claim 2 characterized by carrying out the laminating of the volume phase and transparence conductive layer in contact with an organic luminous layer, and for said volume phase consisting of the fluoride or oxide of alkali metal or alkaline earth metal, and locating said cathode in the range whose thickness is 0.2–10nm.

[Claim 7] Organic electroluminescence devices given in any 1 term of claims 3–6 to which said transparence conductive layer is characterized by being chosen out of the oxide of an indium and/or tin, or a zincic acid ghost. [Claim 8] Organic electroluminescence devices given in any 1 term of claims 2–7 characterized by said anode plate consisting of the metal which has a work function 4.6eV or more.

[Claim 9] Organic electroluminescence devices given in any 1 term of claims 2-8 which the laminating of the high work function metal layer in which said anode plate has a work function 4.6eV or more, and the low resistive layer which has the resistivity below 10-5ohmcm is carried out, and are characterized by the high work function metal layer touching the organic luminous layer.

[Claim 10] Organic electroluminescence devices according to claim 1 characterized by establishing said cathode in the insulating substrate side of an organic electroluminescence cel, establishing said anode plate in the transparence base material side of an organic electroluminescence cel, and having 60% or more of permeability in the light field whose anode plate is 400–800nm.

[Claim 11] Organic electroluminescence devices according to claim 10 to which said anode plate is characterized by being chosen out of the oxide of an indium and/or tin, or a zincic acid ghost.

[Claim 12] Organic electroluminescence devices given in claim 10 which the laminating of the low work function ingredient layer in which said cathode has a work function 4.0eV or less, and the low resistive layer which has the resistivity below 10-50hmcm is carried out, and is characterized by the low work function ingredient layer touching the organic luminous layer thru/or any 1 term of 11.

[Claim 13] Organic electroluminescence devices according to claim 12 to which thickness of said low work function ingredient layer is characterized by being in the range of 2-100nm.

[Claim 14] Organic electroluminescence devices given in any 1 term of claims 12-13 characterized by choosing said low work function ingredient from a Magnesium alloy and an aluminium alloy.

[Claim 15] Organic electroluminescence devices according to claim 10 characterized by carrying out the laminating of the volume phase and transparence conductive layer in contact with an organic luminous layer, and for said volume phase consisting of the fluoride or oxide of alkali metal or alkaline earth metal, and locating said cathode in the range whose thickness is 0.2–10nm.

[Claim 16] Organic electroluminescence devices given in any 1 term of claims 1-15 characterized by said insulating substrate being a glass substrate.

[Claim 17] Organic electroluminescence devices given in any 1 term of claims 1-15 characterized by said insulating substrate being a silicon substrate.

levices given in any 1 term of claims 1-17 to w [Claim 18] Organic electroluminesce said active-matrix circuit part is characterized by being covered with the insulating layer.

[Claim 19] Organic electroluminescence devices given in any 1 term of claims 1-18 characterized by protecting the outside surface of an organic electroluminescence cel by the transparent insulator layer.

[Claim 20] Organic electroluminescence devices according to claim 19 characterized by said transparence insulator layer consisting of an inorganic oxide, inorganic nitrides, or those mixture.

[Claim 21] Organic electroluminescence devices according to claim 19 to 20 characterized by said transparence insulator layer consisting of a fluorine content macromolecule.

[Claim 22] Organic electroluminescence devices given in any 1 term of claims 1-21 characterized by said transparence base material being a glass substrate.

[Claim 23] Organic electroluminescence devices given in any 1 term of claims 1-22 characterized by said luminescence conversion layer consisting of a color filter.

[Claim 24] Organic electroluminescence devices given in any 1 term of claims 1-22 characterized by consisting of the fluorescence conversion layer in which said luminescence conversion layer contains a fluorochrome.

[Claim 25] Organic electroluminescence devices given in any 1 term of claims 1-24 characterized by being in the range whose distance between said insulating substrates and said transparence base materials is 1-20 micrometers.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention] This invention relates to the thin film mold device which emits light, applying electric field to the luminous layer which consists of an organic compound in detail about organic electroluminescence devices. [0002]

[Description of the Prior Art] Although what doped Mn which is an emission center, and rare earth elements (Eu, Ce, Tb, Sm, etc.) is common to ZnS, CaS, SrS, etc. which are the II-VI group compound semiconductor of an inorganic material as an electroluminescence (EL) component of a thin film mold conventionally The EL element produced from the above-mentioned inorganic material has the high (- 200 V) trouble that the cost of difficulty (especially blue) and 4 circumference drive circuits has the high formation of the need (50-1000Hz) and 2 driver voltage 3 having 1 full color alternating current drive.

[0003] However, development of the EL element using an organic thin film came to be performed in recent years for amelioration of the above-mentioned trouble. In order to raise luminous efficiency especially, the class of electrode is optimized for the purpose of the improvement in effectiveness of the carrier impregnation from an electrode, an extensive improvement of luminous efficiency is made as compared with the EL element using single crystals, such as the conventional anthracene, by development (Appl.Phys.Lett., 51 volumes, 913 pages, 1987) of the organic electroluminescence devices which prepared the electron hole transportation layer which consists of aromatic series diamine, and the luminous layer which consists of the aluminum complex of 8-hydroxyquinoline, and the practical use property is approached.

[0004] Besides the electroluminescence devices using the above low-molecular ingredients, as an ingredient of a luminous layer Pori (p-phenylenevinylene) (others [1990 / Nature, 347 volumes, 539 pages, and]), Pori [2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene] (others [1991 / Appl.Phys.Lett., 58 volumes, 1982 pages, and]), Development of the electroluminescence devices using polymeric materials, such as Pori (3-alkyl thiophene) (others [1991 / Jpn.J.Appl.Phys.30 volume, L1938 page, and]), Development of the component (application physics, 61 volumes, 1044 pages, 1992) which mixed a low-molecular luminescent material and a low-molecular electronic transition ingredient to macromolecules, such as a polyvinyl carbazole, is also performed. Moreover, doping fluorochromes for laser, such as a coumarin, by using the aluminum complex of 8-hydroxyquinoline as a host ingredient, for example (J. Appl.Phys.65 volume, 3610 pages, 1989) etc. is performed.

[Problem(s) to be Solved by the Invention] Although a matrix address system (JP,2-66873,A; an institute-of-telecommunications-engineers technical research report, OME89-1989 [46, 37,]) is generally adopted in order to use the above organic electroluminescence devices as a display panel, what (an institute-of-telecommunications-engineers technical research report, OME88-1988 [47, 35,]) brightness decreases with reduction in a duty ratio, and that a cross talk occurs pose a practically big problem with the increment in the number of pixels. Furthermore, it will be necessary to carry out high brightness luminescence momentarily at the time of a dynamic drive, and the increment in driver voltage and decline in power conversion effectiveness will be caused as a result with the increment in the number of the scanning lines.

[0006] In order to solve the problem of this passive-matrix drive method, it is possible to drive organic electroluminescence devices in an active-matrix circuit (JP,6-325869,A; JP,7-122360,A; JP,7-122361,A; JP,7-122362,A; JP,8-54836,A; JP,8-330600,A). However, there is a big trouble about full-color-izing.
[0007] The method which carries out patterning of the :1 organic light emitting device by which some proposals are made, and carries out plane configuration until now according to each luminescent color (RGB) about the method of full-color-izing (Appl.Phys.Lett., 69 volumes, 3117 pages, 1996), 2) The method using minute resonator structure (Jpn.J.Appl.Phys.34 volume, L1234 page, 1995), 3) The method (JP,7-142169,A) which combines a white light emitting device and a color filter, the method (JP,3-152897,A) which combines 4 blue light emitting device and a fluorescence conversion layer, method which carries out the laminating of the 5RGB luminous layer (France patent No. 2,728,082).

[0008] The method of 1) is difficult to apply to a process top organic layer, and has the problem that wavelength shifts with a needing [the method of 2]-expensive half mirror angle of visibility. It will be necessary to take an insulation perpendicularly and wiring will become very complicated about wiring of RGB each luminous layer by making it a laminating mold by the method of 3). 3) And in the method of 4, an organic layer is both the method which a formula can now adopt as a full color panel from the ability to form in solid one.

level beyond a QVGA specification (320x240 d [0009] Since the number of pixels of s assumed, a full color panel becomes an active-matrix drive mold fundamentally. The method of reconciling the ve-mentioned method of 3 and 4 with an active-matrix circuit is required. Until now, by the approach (JP,6-325869,A) currently indicated. the organic electroluminescence cel of each pixel is formed on the same substrate as the component (TFT) of an active-matrix drive circuit, and the luminescence conversion layer (a color filter layer or fluorescence conversion layer) is formed in the outside of a substrate, or the component side. the sectional view in which drawing 1 shows typically the conventional example of structure of general organic electroluminescence devices -- it is -- 1 -- a transparence substrate, and 2-6 - in an anode plate and 9, an organic luminous layer and 10 express cathode and, as for TFT and 7, 11 expresses [a luminescence conversion layer and 8] a tooth-back base material respectively. [0010] However, although the making process of a luminescence conversion layer becomes the TFT formation back, since considering the manufacture process of TFT TFT already formed with developers, such as alkali used at the time of patterning of a luminescence conversion layer, has damage, the protective coat which bears wet process must be formed in a TFT part. since [moreover,] considering the yield as a panel the yield of the whole panel becomes the multiplication of the TFT yield and the luminescence conversion layer yield -- considerable extent -becoming low is expected.

[0011]

[Means for Solving the Problem] The problem of the above-mentioned yield on a production process is a technical problem which must be conquered for implementation of a full color panel. The active-matrix drive to which the manufacture yield of the whole panel does not fall in view of the above-mentioned actual condition is possible for this invention person etc., and it aims at offering the organic electroluminescence devices which can perform a full color display. That is, this inventions are the organic electroluminescence cel which was pinched by an anode plate and cathode and which consists of an organic luminous layer at least, and the organic electroluminescence devices which prepared the active-matrix circuit which drives an organic electroluminescence cel on said substrate, counter with said substrate, arrange a transparence base material at an insulating substrate top, and consist in the organic electroluminescence devices characterized by to prepare the luminescence conversion layer which changes luminescence from an organic electroluminescence cel on said transparence base material.

[Embodiment of the Invention] Hereafter, the organic electroluminescence devices of this invention are explained according to an accompanying drawing. the sectional view showing typically the example of structure of the general organic electroluminescence devices by which drawing 2 is used for this invention — it is — 21 — in a lower electrode and 9, an organic luminous layer and 23 express an up electrode, and, as for a substrate, and 2–6, 24 expresses [TFT and 22] a transparence base material respectively. If a substrate 21 serves as an organic electroluminescence cel and a base material of a TFT part and the process temperature in a TFT production process (membrane formation of amorphous silicon, polycrystalline silicon, CdSe, etc.) is taken into consideration, a thing with the thermal resistance of 200 degrees C or more will be desirable, and the plate of a quartz or glass, a silicon wafer, etc. will be used. When especially a silicon wafer is used, there is an advantage which can form polycrystalline silicon TFT with high definition beforehand. Active-matrix circuits other than TFT are also usable to this invention, for example, the active drive by the metal / insulator / metal (MIM) component is also possible. With amorphous silicon, since process temperature becomes low, a resin substrate can also be used in addition to said substrate. However, since gas barrier property is needed in the case of a resin substrate, it is necessary to prepare the gas barrier layer by silicon oxide, a silicon nitride, etc. at least in one side of a substrate.

[0013] The structure of TFT has shown what is called a reverse stagger mold to <u>drawing 2</u>. It consists of the gate electrode 2, gate dielectric film 3, the semi-conductor layer 4, the ohmic contact layer 5, the source, and the drain electrodes 6a and 6b. Although only TFT of the last stage is shown in <u>drawing 2</u>, in order to carry out the active drive of the organic electroluminescence cel, at least two TFT(s) for switching and one capacitor are required. The concrete example of circuitry is shown in <u>drawing 3</u>. What showed the active drive circuit of <u>drawing 3</u> typically to the plane is shown in <u>drawing 4</u>.

[0014] On a substrate 21, the organic electroluminescence cel which consists of the organic luminous layer 9 inserted into the lower electrode 22 and the up electrode 23 which form each pixel is prepared. Since luminescence from an organic luminescence cel is taken out through an up electrode, an up electrode needs to have 60% or more of permeability in a visible region (400-800nm). In order to obtain luminescence from an organic luminous layer, it is necessary to pour in an electron hole and an electron from each electrode, to make it recombine in an organic luminous layer, and to excite the component of an organic luminous layer. Let an up electrode be cathode in this invention by making into an anode plate the :A. lower electrode which is shown below and with which the approach of two kinds of charge impregnation is devised.

B. Let an up electrode be an anode plate by using a lower electrode as cathode.

Approach A and Approach B — also in any, it is as having mentioned already that it is the need that an up electrode has transparency in a visible region. Hereafter, the component configuration in an all directions method is explained in full detail.

[0015] Since transparency is not required of Approach A lower electrode (anode plate), the metal which usually fills the work function needed for a hole injection is used. The metal which 4.6eV or more is desirable as a value of a work function, and fulfills this value For example, according to the chemistry handbook (edited by Chemical Society of Japan the basic volume II of the 3rd edition, 493-494 pages, Maruzen, 1984) Gold, silver, copper, iridium, molybdenum, nickel, an osmium, Metals and those alloys, such as palladium, platinum, a ruthenium, a

tantalum, and a tungsten, Conductive ymers, such as metallic oxides, such as an oxide subbreviates to ITO below) of an indium and/or tin, copper iodide or polypyrrole, the poly aniline, and Pori (3 monylthiophene), are mentioned. Moreover, in order to lower wiring resistance, it is also possible to carry out the laminating of the above-mentioned metal on other low resistance electrical conducting materials, and to lower the resistance as the whole. 5–1000nm of thickness of a lower electrode is usually about 10–500nm preferably.

[0016] Although a transparent electrode is required as an up electrode (cathode), in order to pour in an electron efficiently, the ingredient which has a work function 4.0eV or less is desirable. However, the work function of a transparence oxide conductor like ITO or ZnO is 4.6eV or more, and it is difficult to use as cathode. Then, the work function ingredient 4.0eV or less was thin-film-ized to extent which has sufficient permeability, it formed on the organic luminous layer, and carrying out the laminating of said transparence electric conduction film on it found out that it was an effective approach. Similarly according to the chemistry handbook, the alloy constituent of metals, such as aluminum, barium, calcium, a cerium, an erbium, europium, a gadolinium, a hafnium, an indium, a lanthanum, magnesium, manganese, neodium, a scandium, samarium, an yttrium, zinc, and a zirconium, and a these metals and the metal with which the work function mentioned previously has the value of 4.6eV or more is used as the aforementioned low work function ingredient 4.0eV or less. moreover, LaB6 etc. — a compound ingredient is also possible for this purpose. 1–100nm of thickness of this low work function ingredient layer is about 0.5–50nm preferably from the request of transparency. The laminating of the transparence conductive layers, such as the above-mentioned ITO and ZnO, is preferably carried out by about 10–500nm 5–1000nm of thickness on this low work function ingredient layer. Since the active drive circuit which has switching and a memory to each lower electrode is formed on the substrate, solid membrane formation is sufficient over [electrode / up] the whole screen product.

[0017] Instead of the above-mentioned low work function ingredient layer, the volume phase which makes easy electron injection from cathode to a luminous layer according to the tunnel obstruction effectiveness may be used. as the ingredient used for this purpose — alkali-metal fluorides, such as LiF and NaF, MgF2, and CaF2 etc. — it consists of the oxide of alkaline earth metal, such as alkali-metal oxides, such as a fluoride of alkaline earth metal, and Li2 O, and MgO, BaO, and since it is these ingredient insulation, as thickness, the range of 0.2-10nm is desirable.

[0018] The vacuum evaporation technique according [the formation approach of a lower electrode and an up electrode] to a resistance heating method or an electron beam method, a sputtering technique, an ECR spatter, the ion beam spatter method, etc. are used. Next, the structure of the organic luminous layer 9 is explained. Although it is also possible to form luminescent material by the monolayer, in order to make luminous efficiency high, the structure which contains an electron hole transportation layer and an electronic transportation layer at least is desirable. Drawing 5 is the sectional view showing typically the example of structure of the general organic electroluminescence cel used for this invention, in a lower electrode (anode plate) and 41, an electron hole transportation layer and 42 express an electronic transportation layer, and 23 expresses [21 / a substrate and 22] an up electrode (cathode) respectively.

[0019] As conditions required of the ingredient of the electron hole transportation layer 41, the hole-injection effectiveness from the lower electrode 22 is high, and it is required to be the ingredient which can convey the poured-in electron hole efficiently. For that purpose, ionization potential is small, from the light of the light, transparency is high, hole mobility is large, it excels in stability further, and, moreover, it is required that it should be hard to generate the impurity used as a trap at the time of manufacture and use. When the application for a mounted display is considered in addition to the above-mentioned general demand, thermal resistance is further required of a component. Therefore, the ingredient which has the value of 70 degrees C or more as Tg is desirable. [0020] The aromatic series diamine compound which connected the 3rd class aromatic amine units, such as 1 and 1-screw (4-G p-tolylamino phenyl) cyclohexane, as such an electron hole transportation ingredient, for example (JP,59-194393,A), The aromatic amine which two or more fused aromatic rings permuted by the nitrogen atom including two or more tertiary amine represented with a 4 and 4'-screw [N-(1-naphthyl)-N-phenylamino] biphenyl (JP,5-234681,A), The aromatic series triamine which has starburst structure with the derivative of triphenyl benzene (U.S. Pat. No. 4,923,774), Aromatic series diamines, such as N, N'-diphenyl-N, and N'-screw (3methylphenyl) biphenyl-4,4'-diamine (U.S. Pat. No. 4,764,625), alpha, alpha, alpha', and alpha'-tetramethyl - alpha and alpha'-screw (4-G p-tolylamino phenyl)-para xylene (JP,3-269084,A), As the whole molecule, a triphenylamine derivative unsymmetrical in three dimensions (JP,4-129271,A), The compound which the aromatic series diamino radical permuted by the pyrenyl radical (JP,4-175395,A), The aromatic series diamine which connected the 3rd class aromatic amine unit by ethylene (JP,4-264189,A), The aromatic series diamine which has styryl structure (JP,4-290851,A), What connected the aromatic series tertiary amine unit by the thiophene radical (JP,4-304466,A), Starburst mold aromatic series triamine (JP,4-308688,A), A benzyl phenyl compound (JP,4-364153,A), the thing which connected tertiary amine by the fluorene radical (JP,5-25473,A), A triamine compound (JP,5-239455,A), a bis-dipyridyl amino biphenyl (JP,5-320634,A), N, N, and N-triphenylamine derivative (JP,6-1972,A). The aromatic series diamine which has phenoxazine structure (JP,7-138562,A). A diamino phenyl phenanthridine derivative (JP,7-252474,A), A hydrazone compound (JP,2-311591,A), a silazane compound (U.S. Pat. No. 4.950,950 official report), a silanamine derivative (JP,6-49079,A), a phosphamine derivative (JP,6-25659,A), the Quinacridone compound, etc. are mentioned. These compounds may be used independently, and if needed, it may mix respectively and they may be used.

[0021] In addition to the above-mentioned compound, as an ingredient of the electron hole transportation layer 41, a

polyvinyl carbazole and polysilane (Applys.Lett., 59 volumes, 2760 pages, 1991), Poly JFAZEN (JP,5-310949,A), a polyamide (JP,5-310949,A), A polyvinyl triphenylamine (JP,7-53953,A), the comolecule which has a triphenylamine frame (JP,4-133065,A), The macromolecule which connected the triphenylamine unit by the methylene group etc. (Synthetic Metals, 55 to 57 volumes, 4163 pages, 1993), Polymeric materials, such as polymethacrylate (J. Polym.Sci., Polym.Chem.Ed., 21 volumes, 969 pages, 1983) containing aromatic amine, are mentioned.

[0022] The electron hole transportation layer 41 is formed by carrying out the laminating of the above-mentioned electron hole transportation ingredient on said lower electrode 22 with the applying method or a vacuum deposition method. In the case of the applying method, additives which do not become a hole trap according to one sort or two sorts or more, and the need about an electron hole transportation ingredient, such as binder resin and a spreading nature amelioration agent, are added, it dissolves, a spreading solution is prepared, and it applies on an anode plate 22 by approaches, such as a spin coat method, and it dries and the electron hole transportation layer 41 is formed. A polycarbonate, polyarylate, polyester, etc. are mentioned as binder resin. Since it will reduce hole mobility if binder resin has many additions, little direction is desirable and its 50 or less % of the weight is usually desirable. [0023] After paying electron hole transportation ingredients to the crucible installed in the vacuum housing and exhausting the inside of a vacuum housing to about 10 - 4Pa with a suitable vacuum pump, in the case of vacuum evaporation technique, a crucible is heated, an electron hole transportation ingredient is evaporated in it, and the electron hole transportation layer 4 is made to form on the anode plate 2 on the substrate 1 which faced each other with the crucible and was placed. When forming the above-mentioned electron hole transportation layer 41, a lowbattery drive can be enabled by doping the metal complex of aromatic carboxylic acid and/or a metal salt (JP,4-320484,A), a benzophenone derivative and a thio benzophenone derivative (JP,5-295361,A), and fullerene (JP,5-331458,A) by 10-3-10% of the weight of concentration, and making the electron hole as a free carrier generate as an acceptor further.

[0024] 10–300nm of thickness of the electron hole transportation layer 41 is usually 30–100nm preferably. In order to form such a thin film uniformly, generally a vacuum deposition method is used well. In order to raise the lower electrode 22 and contact of the electron hole transportation layer 41, as shown in <u>drawing 6</u>, it is possible to form the anode plate buffer layer 40. A thin film with it can be formed, stability, i.e., the melting point, and glass transition temperature are thermally high, and 100 degrees C or more are required as 300 degrees C or more and a glass transition temperature as the melting point. [the good contact to an anode plate and] [uniform as conditions required of the ingredient used for an anode plate buffer layer] Furthermore, it is mentioned that ionization potential is low and the hole injection from an anode plate is easy and that hole mobility is large. Until now for this purpose A porphyrin derivative and a phthalocyanine compound (JP,63–295695,A), Star bust mold aromatic series triamine (JP,4–308688,A), A hydrazone compound (JP,4–320483,A), the aromatic series diamine derivative of an alkoxy permutation (JP,4–220995,A), A p-(9-anthryl)-N and N-G p-tolyl aniline (JP,3–111485,A), Poly thienylene vinylene and Polly p-phenylenevinylene (JP,4–145192,A), Organic compounds, such as the poly aniline (refer to Appl.Phys.Lett., 64 volumes, 1245 pages, and 1994), Metallic oxides (the 43rd applied-physics relation union lecture meeting, 27 a-SY-1996 [9 or]), such as spatter carbon film (JP,8–31573,A), and a banazin san ghost, ruthenium oxide, a molybdic-acid ghost, are reported.

[0025] A porphyrin compound or a phthalocyanine compound is mentioned as a compound often used as the above-mentioned anode plate buffer layer ingredient. These compounds may have the central metal and the thing of a non-metal is sufficient as them. As an example of these desirable compounds, it is :porphin [to which the following compounds are mentioned] 5, 10, and 15, 20-tetrapod phenyl-21H, and 23H-porphin cobalt (II).

5, 10, 15, 20-tetrapod phenyl-21H, and 23H-porphin copper (II)

5, 10, 15, 20-tetrapod phenyl-21H, and 23H-porphin zinc (II)

5, 10, 15, and 20-tetra-phenyl-21 vanadium [H and 23H-porphin] (IV) oxide 5, 10, and 15, 20-tetrapod (4-pyridyl)-21H, 23H-porphin 29H, and 31H-phthalocyanine copper (II) phthalocyanine zinc (II) Phthalocyanine CHITANFUTAROSHIANIN oxide magnesium phthalocyanine lead phthalocyanine copper (II) 4, 4', 4"'-tetraza-29H, and 31H-phthalocyanine [0026] Although thin film formation is possible also for the case of an anode plate buffer layer like an electron hole transportation layer, in the case of an inorganic substance, a spatter, electron beam vacuum deposition, and a plasma-CVD method are used further. 3-100nm of thickness of the anode plate buffer layer 40 formed as mentioned above is usually 10-50nm preferably.

[0027] The electronic transportation layer 42 is formed on the electron hole transportation layer 41. An electronic transportation layer is formed from the compound which can convey the electron from cathode in the direction of an electron hole transportation layer efficiently in inter-electrode [which was able to give electric field]. As an electronic transportability compound used for the electronic transportation layer 42, the electron injection effectiveness from the up electrode (cathode) 23 is high, and it is required to be the compound which can convey the poured-in electron efficiently. For that purpose, to be the compound which the impurity which an electron affinity is large, and electron mobility is moreover large, is further excellent in stability, and serves as a trap cannot generate easily at the time of manufacture and use is demanded.

[0028] As an ingredient which fulfills such conditions, aromatic compounds, such as a tetra-phenyl butadiene (JP,57-51781,A), Metal complexes, such as an aluminum complex of 8-hydroxyquinoline (JP,59-194393,A), The metal complex of a 10-hydroxy benzo[h] quinoline (JP,6-322362,A), a mixed ligand aluminum chelate complex (JP,5-198377,A --) JP,5-198378,A, JP,5-214332,A, a JP,6-172751,A cyclopentadiene derivative (JP,2-289675,A), A peri

diazole derivative (JP,2-216791,A), A bis-sty non derivative (JP,2-289676,A), an nzene derivative (JP.1-245087,A, 2-222484 official report), A perviene derivative (JP.2-189890,A, 3-791 al report), A coumarin compound (JP,2-191694,A, 3-792 official report), A rare earth complex (JP,1-256584,A), a JISUCHIRIRU pyrazine derivative (JP,2-252793,A), p-phenylene compound (JP,3-33183,A), a thiadiazolo pyridine derivative (JP,3-37292,A), A pyrrolo pyridine derivative (JP,3-37293,A), a NAFUCHI lysine derivative (JP,3-203982,A), a silole derivative (03 or 70th spring annual convention [of the Chemical Society of Japan], 2D 1 02, and 2D1 1996), etc. are mentioned. [0029] 10-200nm of thickness of the electronic transportation layer 42 is usually 30-100nm preferably. Although an electronic transportation layer can also be formed by the same approach as an electron hole transportation layer, a vacuum deposition method is usually used. Being the purpose which changes the luminescent color, while raising the luminous efficiency of a component, for example, doping fluorochromes for laser, such as a coumarin, by using the aluminum complex of 8-hydroxyquinoline as a host ingredient (J. Appl.Phys., 65 volumes, 3610 pages, 1989) etc. is performed. As for the advantage of this approach, usable and ** are mentioned also for an usable and 4 filmy fluorochrome with luminous efficiency bad [the fluorochrome from which luminescence wavelength starts adjustable and 3 concentration quenching by selection of improvement and two fluorochromes] by the fluorochrome of one

[0030] Also in the purpose which improves the drive life of a component, it is effective to dope a fluorochrome by using said electronic transportation ingredient as a host ingredient. For example, the luminescence property, especially drive stability of a component can be greatly raised by doping condensed multi-ring aromatic series rings (JP,5-198377,A), such as a naphthacene derivative (JP,4-335087,A) represented by rubrene, the Quinacridone derivative (JP,5-70773,A), and perylene, 0.1 to 10% of the weight to a host ingredient by using metal complexes, such as an aluminum complex of 8-hydroxyquinoline, as a host ingredient.

[0031] As a host ingredient, when the electronic transportation layer 42 plays the role, the above-mentioned electronic transportability compound is mentioned, for example, and when the electron hole transportation layer 41 plays a role of a host ingredient, an above-mentioned aromatic amine compound and an above-mentioned hydrazone compound are mentioned. Although it is doped by homogeneity in the direction of thickness of each class when the above-mentioned dopant is doped in an electron hole transportation layer and/or an electronic transportation layer, there may be concentration distribution in the direction of thickness. For example, it may dope only near the interface with an electron hole transportation layer, or you may dope near the cathode interface conversely. [0032] In this invention, in order to attain full color luminescence, the following two approaches can be considered. One is the approach of making carry out white luminescence of the component, and decomposing the white light into three colors of blue, green, and red, using KARAFIRUTA as a luminescence conversion layer. Three colors of blue, green, and red are obtained by carrying out blue luminescence of the component, and blue's taking out the blue glow in a color as it is by using a fluorescence conversion layer as a luminescence conversion layer, and performing color conversion with a green fluorescence ingredient and a red fluorescence ingredient about green and red as another approach. Therefore, it is necessary to consider as the lamination in which white luminescence or blue luminescence is possible as an organic luminous layer. For this purpose, a luminescence function can be given to for example, an electronic transportation layer, and it can consider as the following lamination.

[0033] As shown in drawing 7, in white luminescence, the electronic transportation layer 42 can be divided into three fields 42a, 42b, and 42c, blue luminous layer 42a, green luminous layer 42b, red luminous layer 42c, then luminescence from each class can pile up and be put together from the direction which touches the electron hole transportation layer 41, and white luminescence can be obtained in it. In order to maintain white color balance, it can do easily by adjusting the thickness of each red luminous layer from blue. It can be used for the host ingredient and pan which are used for the electronic transportation layer mentioned already as an ingredient used for the luminous layer of each color combining dope coloring matter.

[0034] In blue luminescence, blue luminescence can be obtained in the already mentioned electronic transportation layer ingredient according to the host ingredient in which blue fluorescence is shown, and the structure shown in drawing 5 and drawing 6 by forming the electronic transportation layer which doped the blue fluorochrome if needed. As an approach of raising the luminous efficiency of organic electroluminescence devices further, the laminating of the electron injection layer 43 can also be further carried out on the electronic transportation layer 42 (refer to drawing 8). It is required for the compound used for this electron injection layer 43 that the electron injection from cathode should be easy and electronic transport capacity should be still larger. The aluminum complex of the 8-hydroxyquinoline already mentioned as an electronic transportation layer ingredient as such an electronic transportation ingredient, The system which distributed an OKISA diazole derivative (others [1989 / Appl.Phys.Lett., 55 volumes, 1489 pages, and]) and them to resin, such as a polymethyl methacrylate (PMMA), (Appl.Phys.Lett., 61 volumes, 2793 pages, 1992), phenanthroline derivative (JP,5-331459,A), 2-t-butyl -9, 10-N, and N'-dicyano anthraquinone diimine (Phys.Stat.Sol. (a) —) n mold hydrogenation amorphous carbonization silicon, n mold zinc sulfide, n mold zinc selenide, etc. will be mentioned in 142 volumes, 489 pages, and 1994. 5-200nm of thickness of an electron injection layer is usually 10-100nm preferably.

[0035] Since transparency is not required of <Approach B> lower electrode (cathode), the metal which usually fills the work function needed for electron injection is used. Although 4.0eV or less is desirable as a value of a work function, the metal which fulfills this value tends to oxidize, and if an oxide film generates on a front face, electron injection will become difficult in many cases. Moreover, in case patterning of the low work function metal is carried out using wet process, it is thought that neither scaling nor corrosion is avoided. Therefore, as for most parts, it is desirable to form with the metal of low resistance, for example, copper, aluminum, etc., using only the surface part of

a lower electrode as a low work function ingredient layer. 2-100nm of thickness of this look function ingredient layer is about 5-50nm preferably.

[0036] In this case, a low work function ingredient layer can be formed for example, by the vacuum deposition approach. As shown in drawing 2, the source and the drain electrode of TFT for an active drive are covered with the insulating protective coat 12 in order to prevent a short circuit with an up electrode. This insulating protective coat serves as wrap appearance completely except the part of a lower electrode. If a TFT part and this insulating protective coat are doubled, the distance from a lower electrode to the summit of an insulating protective coat will be set to about 3 micrometers. Since the thickness of a low work function ingredient layer is very thin as mentioned above and a level difference piece is easily raised at the wall edge in a vacuum deposition method, only the part on a lower electrode is connected electrically. Since the part formed on the insulating protective coat is in an insulating condition electrically, it does not carry out contribution of what to luminescence, either.

[0037] The ingredient mentioned by Approach A is used as said low work function ingredient. Moreover, the volume phase shown by Approach A can be used instead of the above-mentioned low work function layer. It is Approach A and an ingredient and thickness are already described. Although a transparent electrode is required as an up electrode (anode plate), in order to pour in an electron hole efficiently, the ingredient which has a work function 4.6eV or more is desirable. For this purpose, a transparence oxide electrical conducting material like ITO or ZnO is used. Before forming the up electrode by transparence oxide electric conduction, metals with a more high work function (gold, palladium, etc.) may be formed in the translucent condition, and a component property may be raised.

[0038] Since it is the need that membranes are formed without raising a level difference piece also on the wall side face of the insulating protective coat described previously as the formation approach of an up electrode, the approach of forming membranes with sufficient covering power by whenever [low-vacuum] like a spatter is desirable. The laminating of the up transparence conductive layer is preferably carried out by about 10-500nm 5-1000nm of thickness. Moreover, solid membrane formation is sufficient over [electrode / up] the whole screen product.

[0039] About the structure of the organic luminous layer 9, it becomes the order of a laminating contrary to the lamination stated by Approach A. That is, in the configuration of drawing 5, it becomes the order of a substrate, a lower electrode, an electronic transportation layer, an electron hole transportation layer, and an up electrode. The same is said of the structure of drawing 6 and drawing 7. Finally, the transparence base material 24 with which the luminescence conversion layer 7 and it are formed is explained. In addition to taking out luminescence from an organic electroluminescence cel in support of a luminescence conversion layer, the role of a transparence base material has the function intercepted from the open air for closing a component. Although glass, a quartz, and the resin that carried out the coat of the suitable gas barrier layer are used for this purpose, when a glass plate takes into consideration cost, thermal resistance, and chemical resistance, generally it is desirable.

[0040] About a luminescence conversion layer, two methods are in the appearance mentioned already. In combining with a white light emitting device, it forms a color filter on said transparence base material with a black matrix. There are not a color filter technique of existing [the formation approach] and a place which changes in any way. In the case of a fluorescence conversion layer, what distributed the fluorochrome to the resin medium instead of the pigment is used. It is also possible to give the function of a color filter to fluorescence conversion and coincidence. [0041] Although the transparence base material with which the insulating substrate which was produced as mentioned above, and which supports organic electroluminescence devices, and the luminescence conversion layer were formed is intercepted from the open air with a suitable spacer, heat curing, or photo-curing resin and the closure is carried out, it is desirable to use a thing with a size of 1-20 micrometers as a spacer in that case, and to specify the distance between an insulating substrate and a transparence base material. In the distance of less than 1 micro, damage may be done to a component in the case of handling, and a horizontal location gap of the luminescence conversion layer on a part for the light-emitting part which organic electroluminescence devices form with an angle of visibility, and a transparence base material occurs in the distance of 20 micro or more. [0042]

[Example] Next, although an example explains this invention still more concretely, this invention is not limited to the publication of the following examples, unless the summary is exceeded. The example of manufacture of organic electroluminescence devices is shown below.

[0043] Example 1 (approach A)

According to Approach A, the component was produced in the process shown below. As a design of a TFT component, in the circuit diagram shown in <u>drawing 3</u>, gate length of the 1st TFT was made into 20 microns, gate width was made into 100 microns, gate length of the 2nd TFT was made into 20 microns, and gate width was made into 600 microns. Pixel area is 600 micron x600 micron, pixel spacing is 800 micron x800 micron, and the numerical aperture was made into 56%.

[0044] Each manufacture process is explained according to drawing 8 below.

(a) Patterning of the gate electrode which reaches what carried out the laminating of the Au by 20nm of thickness on aluminum film further what carried out vacuum deposition of the aluminum with the resistance heating method by 200nm of thickness lower electrode (anode plate) 22 with a usual photolithography technique and a usual wet etching technique on a lower electrode and a gate electrode formation process alkali-free-glass (7059 by Corning, Inc.) substrate was performed. It was 4.8eV when the work function of this lower electrode (anode plate) was measured by the Riken Keiki tabulation side analysis apparatus (AC-1).

[0045] (b) Gate dielectric film, the supposed conductor layer, and the substrate produced at the hmic contact layer membrane formation process process (a) were set in plasma-CVD equipment, and continuation membrane formation of each class 3b, 4b, and 5b was carried out on the conditions shown in the following table -1.
[0046]

[Table 1]

成膜条件	1.SiNx 雇	2. i層a-Si	3.n ⁺ 産a-Si	
<ガス流量>				
SiH4	10	20	10	
NH3	100	_	-	
H2		20	_	
PH3/H2 (0.1%)		1-2	100	
基板温度【で】	300	280	280	
成膜圧力 [Torr]	0.25	0.15	0.33	
電力密度 [W/cm²]	0.14	0.08	0.08	
減厚 [nm]	300	100 -	50	

[0047] (c) Pick out a substrate from the plasma-CVD equipment of the a-Si patterning process above, and it is a usual photolithography technique and usual SF6. Plasma etching using gas performed patterning of a-Si. (d) By the source, and drain electrode formation process usual a photolithography technique and electron beam evaporation, the drain and source electrode which carried out the laminating of 50nm Cr layer and the 100nm aluminum layer one by one were formed.

[0048] (e) n+a-Si layer dirty off process usual a photolithography technique and SF6 By plasma etching using gas, the layer of n+a-Si was etched by having used the source and a drain electrode as the mask, and the channel was formed. When the property of a-SiTFT of the organic electroluminescence panel produced at the above-mentioned process (a) - the process (e) was evaluated, mobility (micro FE) was 0.5cm2 / V-sec, and the threshold was 3V. [0049] (f) The insulating layer of 1.3 micrometers of thickness was formed with the usual photolithography technique using the insulator layer formation process alkali development mold transparence heatproof resist ingredient for active-matrix circuit protection (the product made from Nippon Steel Chemistry; V-259PA).

(g) Organic electroluminescence layer membrane formation process (white luminescence cel)

After ultrasonic cleaning and pure water performed the drive circuit board done even at the process (f) by isopropyl alcohol and rinsing and desiccation nitrogen performed desiccation, and UV / ozone washing, the adhesion mask which limits a vacuum evaporation part was attached, and it installed in the vacuum evaporation system, and it exhausted using the oil diffusion pump until the degree of vacuum in equipment was set to 2x10 to 6 or less Torrs. [0050] The organic electroluminescence—devices part which has hereafter the white luminescence function of the structure shown in drawing 7 was produced. It vapor—deposited by heating the copper phthalocyanine (H1) (crystal form being beta mold) shown in the following put into the molybdenum boat arranged in the above—mentioned vacuum devices. It vapor—deposited with degree of vacuum 2x10-6Torr (about 2.7x10 to 4 Pa), and the evaporation rate of 0.3nm/second, and the anode plate buffer layer 40 of 20nm of thickness was obtained. [0051]

[Formula 1]

[0052] Next, it is the periphery [0053] of a crucible about the 4 and 4'-screw [N-(1-naphthyl)-N-phenylamino] biphenyl (H2) shown in the following put into the ceramic crucible arranged in said equipment. [Formula 2]

[0054] It vapor-deposited by heating at the tantalum wire heater of an enclosure. The temperature of the end crater which gets at this time was controlled in 250-260 degrees C. The electron hole transportation layer 41 of 60nm of thickness was obtained with degree of vacuum 1.7x10-6Torr at the time of vacuum evaporationo (about 2.3x10 to 4 Pa), and the evaporation rate of 0.3-0.5nm/second. The range of crucible temperature is 200-210 degrees C about the zinc OKISA diazole complex (E1) shown in the following structure expressions as an ingredient of electronic transportation layer 42a which has a blue luminescence function, and it is ** [0055]. [Formula 3]

[0056] It drove, and the degree of vacuum at the time of vacuum evaporation was 1.5x10-6Torr (about 2.0x10 to 4 Pa), the evaporation rate was 0.2-0.3nm/second, and the thickness of the vapor-deposited blue luminous layer was 30nm. Next, the 8-hydroxyquinoline complex (E2) of the aluminum shown below was similarly vapor-deposited as an ingredient which forms green luminous layer 42b. Controlling the end-crater temperature which gets at this time in 270-300 degrees C, the degree of vacuum at the time of vacuum evaporationo carried out the laminating of 1.5x10-6Torr (about 2.0x10 to 4 Pa), and the evaporation rate on blue luminous layer 42a by 0.1-0.2nm /and 15nm of thickness a second.

[0057] 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)- which shows the 8-hydroxyquinoline complex (E2) of aluminum for red luminous layer 42c in the following structure expressions as dope coloring matter as a host ingredient as the last of a luminous layer — it used the 4H-pyran (DCM) (D1).
[0058]

[0059] The range of the crucible temperature of the 8-hydroxyquinoline complex of the aluminum at this time is 270−300 degrees C, the crucible temperature of DCM was controlled in 100−110 degrees C, the degree of vacuum at the time of vacuum evaporationo is 1.3x10-6Torr (about 1.7x10 to 4 Pa), an evaporation rate is 0.1nm/second, and the laminating was carried out on green luminous layer 42c by 15nm of thickness. The amount which DCM contained in the 8-hydroxyquinoline complex of aluminum was 2 % of the weight. The substrate temperature when carrying out vacuum deposition of the above-mentioned anode plate buffer layer 40, the electron hole transportation layer 41, and each electronic transportation layers 42a-42c was held to the room temperature. [0060] (h) an up electrode formation process — here, after exchanging the component which performed the vacuum evaporationo to the electronic transportation layer 42 for the shadow mask which specifies the vacuum evaporationo field and electrode takeoff connection of an up electrode, it was made to stick to a component, and it exhausted until it installed in another vacuum evaporation system and the degree of vacuum in equipment became below 2x10-6Torr (about 2.7x10 to 4 Pa) like the organic layer. Then, as cathode 4, the alloy electrode of magnesium and silver was vapor-deposited so that 2 yuan might become 20nm of thickness with coincidence vacuum deposition. Vacuum evaporationo was performed using the molybdenum boat in degree of vacuum 5x10-6Torr (about 6.7x10 to 4 Pa), and vacuum evaporationo time amount 3 minutes and 20 seconds. Moreover, the atomic ratio of magnesium and silver was set to 10:1.4. The work function of the Magnesium alloy of this presentation was 3.6eV. Then, the component was moved to the sputtering system, the laminating of the ITO film was carried out on magnesium and the silver alloy film by 150nm thickness, and the up electrode 23 was completed.

By the usual RF magnetron sputteril and thod, the component performed the spatter, which theating. As spatter conditions for ITO, the mixed gas (0.1% of oxygen densities) of argon-oxygen, pressure 3 Torr (about 0.4Pa), power-flux-density 0.1 W/cm2, a target, and distance between substrates were set to 10cm, in order to prevent a plasma damage. The work function of the ITO film obtained as mentioned above was 4.7eV.

[0061] (i) It is a target within the still more nearly same sputtering system on the component which even the protective coat formation process up electrode formed SiO2 It carries out and is transparent SiO2. The protective coat was formed by 1000nm of thickness.

(j) The component ended to the closure process process (i) was taken out in the box permuted with dry nitrogen, TFT and the organic luminescence cel substrate which applied the photo-setting resin to the periphery for the glass substrate which carried out patterning of the color filter (blue, green, red) so that it might be in agreement with the electrode pattern of an organic electroluminescence cel as a luminescence conversion layer beforehand, and after the marker performed alignment, UV exposure was carried out and hardening processing was completed. At this time, the distance of an organic luminescence cel substrate and a color filter substrate was set up with 5 micrometers by making photo-curing resin distribute a silica bead with a diameter of 5 micrometers. The color filter was formed using the color resist according to the approach usually learned, the transparence smoothing layer was prepared on it, and all thickness could be 3 micrometers.

[0062] When the organic electroluminescence devices completed at the above-mentioned process were made to drive, luminescence of green [which were changed in each color filter layer / the red and green], and blue has been checked. Moreover, the full color image has been attained by carrying out gradation control of blue, green, and the luminescence brightness of each red subpixel.

Example 2 (approach B)

According to Approach B, the component was produced in the process shown below. The design of a TFT component is the same as an example 1. Each manufacture process is explained according to <u>drawing 8</u> below. (a') A usual photolithography technique and a usual wet etching technique performed patterning of the lower electrode (cathode) 22 and a gate electrode for what formed Cr for aluminum by the sputtering method by 50nm of thickness further 200nm of thickness on the lower electrode and the gate electrode formation process alkali—free—glass (7059 by Corning, Inc.) substrate.

[0063] A process (b) - a process (f) are performed like an example 1.

(g') Organic electroluminescence layer membrane formation process (blue luminescence cel)

Then, the low work function layer of a lower electrode (cathode) was formed by the following approaches. After ultrasonic cleaning and pure water performed the drive circuit board done even at the process (f) by isopropyl alcohol and rinsing and desiccation nitrogen performed desiccation, and UV / ozone washing, the shadow mask which specifies a vacuum evaporationo field and an electrode takeoff connection was stuck for the component, and it exhausted until it installed in the vacuum evaporation system and the degree of vacuum in equipment became below 2x10-6Torr (about 2.7x10 to 4 Pa) like the organic layer. As a low work function layer of a lower electrode, the alloy electrode of magnesium and silver was vapor-deposited so that 2 yuan might become 50nm of thickness with coincidence vacuum deposition. The work function of this Magnesium alloy was 3.6eV.

[0064] The organic electroluminescence-devices part which has hereafter the white luminescence function of the structure shown in <u>drawing 8</u> was produced. The anode plate buffer layers 40 and 4 of 20nm of thickness which consists of a copper phthalocyanine (H1), and the electron hole transportation layer 41 of 60nm of thickness which consists of a 4'-screw [N-(1-naphthyl)-N-phenylamino] biphenyl (H2) were formed like the making process of an example 1. Next, the aluminum 2 angle complex (E1) of the 2-methyl-8-hydroxyquinoline shown in the following structure expressions as a host ingredient of the electronic transportation layer 42 which has a blue luminescence function and [0065]

[Formula 5]

[0066] About the perylene (D2) shown in the following structure expressions as dope coloring matter, it is a separate crucible [0067] respectively.

[Formula 6]

[0068] ******* vacuum evaporation 2 yuan was performed. The range of the crucial emperature of the aluminum 2 nucleus complex at this time is 300-320 degrees C, the crucible temperature perylene was controlled in 110-120 degrees C, the degree of vacuum at the time of vacuum evaporation is 1.8x10-6Torr (about 2.4x10 to 4 Pa), an evaporation rate is 0.2-0.3nm/second, and the laminating of the blue luminous layer of 45nm of thickness was carried out on the electron hole transportation layer 41.

[0069] Finally, the 8-hydroxyquinoline complex (E2) of aluminum was used as an electron injection layer. The crucible temperature of the 8-hydroxyquinoline complex of the aluminum at this time was controlled in 270-280 degrees C, the degree of vacuum at the time of vacuum evaporationo is 1.3x10-6Torr (about 1.7x10 to 4 Pa), an evaporation rate is 0.2-0.3nm/second, and the laminating of the electron injection layer of 30nm of thickness was carried out on the electronic transportation layer. The substrate temperature when carrying out vacuum deposition of the anode plate buffer layer 40, the electron hole transportation layer 41, the above-mentioned electronic transportation layer 42, and the above-mentioned electron injection layer 43 was held to the room temperature. [0070] (h') The ITO film was formed by 150nm thickness as an up electrode formation process, then an up electrode (anode plate). By the usual RF magnetron sputtering method, the component performed the spatter, without heating. As spatter conditions for ITO, the mixed gas (0.1% of oxygen densities) of argon-oxygen, pressure 3x10-3Torr (about 0.4Pa), power-flux-density 0.1 W/cm2, a target, and distance between substrates were set to 10cm, in order to prevent a plasma damage. The work function of this anode plate was 4.7eV.

[0071] Then, after passing through a protective coat formation process (i), the fluorescence conversion layer was used as a luminescence conversion layer, and also the closure process (j) as well as an example 1 was performed, and the stroke was made to complete like Approach A. Since blue luminescence was used as it was as a fluorescence conversion layer, it was unnecessary, and after distributing a coumarin 6 and distributing phenoxazone 660 for the thing which made PMMA distribute a coumarin 6 3% of the weight about a green fluorescence conversion layer 2% of the weight in PMMA 1% of the weight as a red fluorescence conversion layer, the laminating of the transparence smoothing layer was carried out, and it formed by 3 micrometers of all thickness.

[0072] When the organic electroluminescence devices completed at the above-mentioned process were made to drive, luminescence of the clear red changed in each fluorescence conversion layer, green, and blue has been checked.

[0073]

[Effect of the Invention] While being able to offer the organic electroluminescence devices which have the display capacity which was excellent by forming the insulating substrate in which the active-matrix circuit and the organic electroluminescence cel were formed, and the transparence support substrate which prepared the luminescence conversion layer face to face in this invention, the yield is good and can manufacture the advantageous panel also in cost. Therefore, the organic electroluminescence panel of this invention can consider the application to the field of a flat-panel display (for example, the object for OA, the object for FA and the computer for LA, and a flat TV), or the display panel of measuring machine machines, and the technical value is large.



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TECHNICAL FIELD

[Field of the Invention] This invention relates to the thin film mold device which emits light, applying electric field to the luminous layer which consists of an organic compound in detail about organic electroluminescence devices.



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PRIOR ART

[Description of the Prior Art] Although what doped Mn which is an emission center, and rare earth elements (Eu, Ce, Tb, Sm, etc.) is common to ZnS, CaS, SrS, etc. which are the II-VI group compound semiconductor of an inorganic material as an electroluminescence (EL) component of a thin film mold conventionally The EL element produced from the above-mentioned inorganic material has the high (- 200 V) trouble that the cost of difficulty (especially blue) and 4 circumference drive circuits has the high formation of the need (50-1000Hz) and 2 driver voltage 3 having 1 full color alternating current drive.

[0003] However, development of the EL element using an organic thin film came to be performed in recent years for amelioration of the above-mentioned trouble. In order to raise luminous efficiency especially, the class of electrode is optimized for the purpose of the improvement in effectiveness of the carrier impregnation from an electrode, an extensive improvement of luminous efficiency is made as compared with the EL element using single crystals, such as the conventional anthracene, by development (Appl.Phys.Lett., 51 volumes, 913 pages, 1987) of the organic electroluminescence devices which prepared the electron hole transportation layer which consists of aromatic series diamine, and the luminous layer which consists of the aluminum complex of 8-hydroxyquinoline, and the practical use property is approached.

[0004] Besides the electroluminescence devices using the above low-molecular ingredients, as an ingredient of a luminous layer Pori (p-phenylenevinylene) (others [1990 / Nature, 347 volumes, 539 pages, and]), Pori [2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene] (others [1991 / Appl.Phys.Lett., 58 volumes, 1982 pages, and]), Development of the electroluminescence devices using polymeric materials, such as Pori (3-alkyl thiophene) (others [1991 / Jpn.J.Appl.Phys.30 volume, L1938 page, and]), Development of the component (application physics, 61 volumes, 1044 pages, 1992) which mixed a low-molecular luminescent material and a low-molecular electronic transition ingredient to macromolecules, such as a polyvinyl carbazole, is also performed. Moreover, doping fluorochromes for laser, such as a coumarin, by using the aluminum complex of 8-hydroxyquinoline as a host ingredient, for example (J. Appl.Phys.65 volume, 3610 pages, 1989) etc. is performed.



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EFFECT OF THE INVENTION

[Effect of the Invention] While being able to offer the organic electroluminescence devices which have the display capacity which was excellent by forming the insulating substrate in which the active-matrix circuit and the organic electroluminescence cel were formed, and the transparence support substrate which prepared the luminescence conversion layer face to face in this invention, the yield is good and can manufacture the advantageous panel also in cost. Therefore, the organic electroluminescence panel of this invention can consider the application to the field of a flat-panel display (for example, the object for OA, the object for FA and the computer for LA, and a flat TV), or the display panel of measuring machine machines, and the technical value is large.



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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although a matrix address system (JP,2-66873,A; an institute-of-telecommunications-engineers technical research report, OME89-1989 [46, 37,]) is generally adopted in order to use the above organic electroluminescence devices as a display panel, what (an institute-of-telecommunications-engineers technical research report, OME88-1988 [47, 35,]) brightness decreases with reduction in a duty ratio, and that a cross talk occurs pose a practically big problem with the increment in the number of pixels. Furthermore, it will be necessary to carry out high brightness luminescence momentarily at the time of a dynamic drive, and the increment in driver voltage and decline in power conversion effectiveness will be caused as a result with the increment in the number of the scanning lines.

[0006] In order to solve the problem of this passive-matrix drive method, it is possible to drive organic electroluminescence devices in an active-matrix circuit (JP,6-325869,A; JP,7-122360,A; JP,7-122361,A; JP,7-122362,A; JP,8-54836,A; JP,8-330600,A). However, there is a big trouble about full-color-izing.
[0007] The method which carries out patterning of the :1 organic light emitting device by which some proposals are made, and carries out plane configuration until now according to each luminescent color (RGB) about the method of full-color-izing (Appl.Phys.Lett., 69 volumes, 3117 pages, 1996), 2) The method using minute resonator structure (Jpn.J.Appl.Phys.34 volume, L1234 page, 1995), 3) The method (JP,7-142169,A) which combines a white light emitting device and a color filter, the method (JP,3-152897,A) which combines 4 blue light emitting device and a fluorescence conversion layer, method which carries out the laminating of the 5RGB luminous layer (France patent No. 2,728,082).

[0008] The method of 1) is difficult to apply to a process top organic layer, and has the problem that wavelength shifts with a needing [the method of 2]-expensive half mirror angle of visibility. It will be necessary to take an insulation perpendicularly and wiring will become very complicated about wiring of RGB each luminous layer by making it a laminating mold by the method of 3). 3) And in the method of 4, an organic layer is both the method which a formula can now adopt as a full color panel from the ability to form in solid one.

[0009] Since the number of pixels of the level beyond a QVGA specification (320x240 dots) is assumed, a full color panel becomes an active-matrix drive mold fundamentally. The method of reconciling the above-mentioned method of 3 and 4 with an active-matrix circuit is required. Until now, by the approach (JP,6-325869,A) currently indicated, the organic electroluminescence cel of each pixel is formed on the same substrate as the component (TFT) of an active-matrix drive circuit, and the luminescence conversion layer (a color filter layer or fluorescence conversion layer) is formed in the outside of a substrate, or the component side, the sectional view in which drawing 1 shows typically the conventional example of structure of general organic electroluminescence devices — it is — 1 — a transparence substrate, and 2-6 — in an anode plate and 9, an organic luminous layer and 10 express cathode and, as for TFT and 7, 11 expresses [a luminescence conversion layer and 8] a tooth-back base material respectively. [0010] However, although the making process of a luminescence conversion layer becomes the TFT formation back, since considering the manufacture process of TFT TFT already formed with developers, such as alkali used at the time of patterning of a luminescence conversion layer, has damage, the protective coat which bears wet process must be formed in a TFT part, since [moreover,] considering the yield as a panel the yield of the whole panel becomes the multiplication of the TFT yield and the luminescence conversion layer yield — considerable extent — becoming low is expected.



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MEANS

[Means for Solving the Problem] The problem of the above-mentioned yield on a production process is a technical problem which must be conquered for implementation of a full color panel. The active-matrix drive to which the manufacture yield of the whole panel does not fall in view of the above-mentioned actual condition is possible for this invention person etc., and it aims at offering the organic electroluminescence devices which can perform a full color display. That is, this inventions are the organic electroluminescence cel which was pinched by an anode plate and cathode and which consists of an organic luminous layer at least, and the organic electroluminescence devices which prepared the active-matrix circuit which drives an organic electroluminescence cel on said substrate, counter with said substrate, arrange a transparence base material at an insulating substrate top, and consist in the organic electroluminescence devices characterized by to prepare the luminescence conversion layer which changes luminescence from an organic electroluminescence cel on said transparence base material.

[0012]

[Embodiment of the Invention] Hereafter, the organic electroluminescence devices of this invention are explained according to an accompanying drawing. the sectional view showing typically the example of structure of the general organic electroluminescence devices by which drawing 2 is used for this invention — it is — 21 — in a lower electrode and 9, an organic luminous layer and 23 express an up electrode, and, as for a substrate, and 2–6, 24 expresses [TFT and 22] a transparence base material respectively. If a substrate 21 serves as an organic electroluminescence cel and a base material of a TFT part and the process temperature in a TFT production process (membrane formation of amorphous silicon, polycrystalline silicon, CdSe, etc.) is taken into consideration, a thing with the thermal resistance of 200 degrees C or more will be desirable, and the plate of a quartz or glass, a silicon wafer, etc. will be used. When especially a silicon wafer is used, there is an advantage which can form polycrystalline silicon TFT with high definition beforehand. Active—matrix circuits other than TFT are also usable to this invention, for example, the active drive by the metal / insulator / metal (MIM) component is also possible. With amorphous silicon, since process temperature becomes low, a resin substrate can also be used in addition to said substrate. However, since gas barrier property is needed in the case of a resin substrate, it is necessary to prepare the gas barrier layer by silicon oxide, a silicon nitride, etc. at least in one side of a substrate.

[0013] The structure of TFT has shown what is called a reverse stagger mold to <u>drawing 2</u>. It consists of the gate electrode 2, gate dielectric film 3, the semi-conductor layer 4, the ohmic contact layer 5, the source, and the drain electrodes 6a and 6b. Although only TFT of the last stage is shown in <u>drawing 2</u>, in order to carry out the active drive of the organic electroluminescence cel, at least two TFT(s) for switching and one capacitor are required. The concrete example of circuitry is shown in <u>drawing 3</u>. What showed the active drive circuit of <u>drawing 3</u> typically to the plane is shown in <u>drawing 4</u>.

[0014] On a substrate 21, the organic electroluminescence cel which consists of the organic luminous layer 9 inserted into the lower electrode 22 and the up electrode 23 which form each pixel is prepared. Since luminescence from an organic luminescence cel is taken out through an up electrode, an up electrode needs to have 60% or more of permeability in a visible region (400–800nm). In order to obtain luminescence from an organic luminous layer, it is necessary to pour in an electron hole and an electron from each electrode, to make it recombine in an organic luminous layer, and to excite the component of an organic luminous layer. Let an up electrode be cathode in this invention by making into an anode plate the :A. lower electrode which is shown below and with which the approach of two kinds of charge impregnation is devised.

B. Let an up electrode be an anode plate by using a lower electrode as cathode.

Approach A and Approach B — also in any, it is as having mentioned already that it is the need that an up electrode has transparency in a visible region. Hereafter, the component configuration in an all directions method is explained in full detail.

[0015] Since transparency is not required of <Approach A> lower electrode (anode plate), the metal which usually fills the work function needed for a hole injection is used. The metal which 4.6eV or more is desirable as a value of a work function, and fulfills this value For example, according to the chemistry handbook (edited by Chemical Society of Japan the basic volume II of the 3rd edition, 493-494 pages, Maruzen, 1984) Gold, silver, copper, iridium, molybdenum, niobium, nickel, an osmium, Metals and those alloys, such as palladium, platinum, a ruthenium, a tantalum, and a tungsten, Conductive polymers, such as metallic oxides, such as an oxide (it abbreviates to ITO below) of an indium and/or tin, copper iodide or polypyrrole, the poly aniline, and Pori (3-methylthiophene), are mentioned. Moreover, in order to lower wiring resistance, it is also possible to carry out the laminating of the abovementioned metal on other low resistance electrical conducting materials, and to lower the resistance as the whole.

de is usually about 10-500nm preferably. 5-1000nm of thickness of a lower el [0016] Although a transparent electrode is required as an up electrode (cathode), in orde pour in an electron efficiently, the ingredient which has a work function 4.0eV or less is desirable. However, the work function of a transparence oxide conductor like ITO or ZnO is 4.6eV or more, and it is difficult to use as cathode. Then, the work function ingredient 4.0eV or less was thin-film-ized to extent which has sufficient permeability, it formed on the organic luminous layer, and carrying out the laminating of said transparence electric conduction film on it found out that it was an effective approach. Similarly according to the chemistry handbook, the alloy constituent of metals, such as aluminum, barium, calcium, a cerium, an erbium, europium, a gadolinium, a hafnium, an indium, a lanthanum, magnesium, manganese, neodium, a scandium, samarium, an yttrium, zinc, and a zirconium, and a these metals and the metal with which the work function mentioned previously has the value of 4.6eV or more is used as the aforementioned low work function ingredient 4.0eV or less. moreover, LaB6 etc. — a compound ingredient is also possible for this purpose. 1-100nm of thickness of this low work function ingredient layer is about 0.5-50nm preferably from the request of transparency. The laminating of the transparence conductive layers, such as the above-mentioned ITO and ZnO, is preferably carried out by about 10-500nm 5-1000nm of thickness on this low work function ingredient layer. Since the active drive circuit which has switching and a memory to each lower electrode is formed on the substrate, solid membrane formation is sufficient over [electrode / up] the whole screen product.

[0017] Instead of the above-mentioned low work function ingredient layer, the volume phase which makes easy electron injection from cathode to a luminous layer according to the tunnel obstruction effectiveness may be used. as the ingredient used for this purpose — alkali-metal fluorides, such as LiF and NaF, MgF2, and CaF2 etc. — it consists of the oxide of alkaline earth metal, such as alkali-metal oxides, such as a fluoride of alkaline earth metal, and Li2 O, and MgO, BaO, and since it is these ingredient insulation, as thickness, the range of 0.2-10nm is desirable.

[0018] The vacuum evaporation technique according [the formation approach of a lower electrode and an up electrode] to a resistance heating method or an electron beam method, a sputtering technique, an ECR spatter, the ion beam spatter method, etc. are used. Next, the structure of the organic luminous layer 9 is explained. Although it is also possible to form luminescent material by the monolayer, in order to make luminous efficiency high, the structure which contains an electron hole transportation layer and an electronic transportation layer at least is desirable. Drawing 5 is the sectional view showing typically the example of structure of the general organic electroluminescence cel used for this invention, in a lower electrode (anode plate) and 41, an electron hole transportation layer and 42 express an electronic transportation layer, and 23 expresses [21 / a substrate and 22] an up electrode (cathode) respectively.

[0019] As conditions required of the ingredient of the electron hole transportation layer 41, the hole-injection effectiveness from the lower electrode 22 is high, and it is required to be the ingredient which can convey the poured-in electron hole efficiently. For that purpose, ionization potential is small, from the light of the light, transparency is high, hole mobility is large, it excels in stability further, and, moreover, it is required that it should be hard to generate the impurity used as a trap at the time of manufacture and use. When the application for a mounted display is considered in addition to the above-mentioned general demand, thermal resistance is further required of a component. Therefore, the ingredient which has the value of 70 degrees C or more as Tg is desirable. [0020] The aromatic series diamine compound which connected the 3rd class aromatic amine units, such as 1 and 1-screw (4-G p-tolylamino phenyl) cyclohexane, as such an electron hole transportation ingredient, for example (JP,59-194393,A), The aromatic amine which two or more fused aromatic rings permuted by the nitrogen atom including two or more tertiary amine represented with a 4 and 4'-screw [N-(1-naphthyl)-N-phenylamino] biphenyl (JP,5-234681,A), The aromatic series triamine which has starburst structure with the derivative of triphenyl benzene (U.S. Pat. No. 4,923,774), Aromatic series diamines, such as N, N'-diphenyl-N, and N'-screw (3methylphenyl) biphenyl-4,4'-diamine (U.S. Pat. No. 4,764,625), alpha, alpha, alpha', and alpha'-tetramethyl - alpha and alpha'-screw (4-G p-tolylamino phenyl)-para xylene (JP,3-269084,A), As the whole molecule, a triphenylamine derivative unsymmetrical in three dimensions (JP,4-129271,A), The compound which the aromatic series diamino radical permuted by the pyrenyl radical (JP,4-175395,A), The aromatic series diamine which connected the 3rd class aromatic amine unit by ethylene (JP,4-264189,A), The aromatic series diamine which has styryl structure (JP,4-290851,A), What connected the aromatic series tertiary amine unit by the thiophene radical (JP,4-304466,A), Starburst mold aromatic series triamine (JP,4-308688,A), A benzyl phenyl compound (JP,4-364153,A), the thing which connected tertiary amine by the fluorene radical (JP,5-25473,A), A triamine compound (JP,5-239455,A), a bis-dipyridyl amino biphenyl (JP,5-320634,A), N, N, and N-triphenylamine derivative (JP,6-1972,A), The aromatic series diamine which has phenoxazine structure (JP,7−138562,A), A diamino phenyl phenanthridine derivative (JP,7− 252474,A), A hydrazone compound (JP,2−311591,A), a silazane compound (U.S. Pat. No. 4,950,950 official report), a silanamine derivative (JP,6-49079,A), a phosphamine derivative (JP,6-25659,A), the Quinacridone compound, etc. are mentioned. These compounds may be used independently, and if needed, it may mix respectively and they may be used.

[0021] In addition to the above-mentioned compound, as an ingredient of the electron hole transportation layer 41, a polyvinyl carbazole and polysilane (Appl.Phys.Lett., 59 volumes, 2760 pages, 1991), Poly FOSUFAZEN (JP,5-310949,A), a polyamide (JP,5-310949,A), A polyvinyl triphenylamine (JP,7-53953,A), the macromolecule which has a triphenylamine frame (JP,4-133065,A), The macromolecule which connected the triphenylamine unit by the methylene group etc. (Synthetic Metals, 55 to 57 volumes, 4163 pages, 1993), Polymeric materials, such as

polymethacrylate (J. Polym.Sci., Polymem.Ed., 21 volumes, 969 pages, 1983) containing matic amine, are mentioned.

[0022] The electron hole transportation layer 41 is formed by carrying out the laminating of the above-mentioned electron hole transportation ingredient on said lower electrode 22 with the applying method or a vacuum deposition method. In the case of the applying method, additives which do not become a hole trap according to one sort or two sorts or more, and the need about an electron hole transportation ingredient, such as binder resin and a spreading nature amelioration agent, are added, it dissolves, a spreading solution is prepared, and it applies on an anode plate 22 by approaches, such as a spin coat method, and it dries and the electron hole transportation layer 41 is formed, A polycarbonate, polyarylate, polyester, etc. are mentioned as binder resin. Since it will reduce hole mobility if binder resin has many additions, little direction is desirable and its 50 or less % of the weight is usually desirable. [0023] After paying electron hole transportation ingredients to the crucible installed in the vacuum housing and exhausting the inside of a vacuum housing to about 10 – 4Pa with a suitable vacuum pump, in the case of vacuum evaporation technique, a crucible is heated, an electron hole transportation ingredient is evaporated in it, and the electron hole transportation layer 4 is made to form on the anode plate 2 on the substrate 1 which faced each other with the crucible and was placed. When forming the above-mentioned electron hole transportation layer 41, a lowbattery drive can be enabled by doping the metal complex of aromatic carboxylic acid and/or a metal salt (JP.4-320484,A), a benzophenone derivative and a thio benzophenone derivative (JP,5-295361,A), and fullerene (JP,5-331458,A) by 10−3 − 10% of the weight of concentration, and making the electron hole as a free carrier generate as an acceptor further.

[0024] 10–300nm of thickness of the electron hole transportation layer 41 is usually 30–100nm preferably. In order to form such a thin film uniformly, generally a vacuum deposition method is used well. In order to raise the lower electrode 22 and contact of the electron hole transportation layer 41, as shown in <u>drawing 6</u>, it is possible to form the anode plate buffer layer 40. A thin film with it can be formed, stability, i.e., the melting point, and glass transition temperature are thermally high, and 100 degrees C or more are required as 300 degrees C or more and a glass transition temperature as the melting point. [the good contact to an anode plate and] [uniform as conditions required of the ingredient used for an anode plate buffer layer] Furthermore, it is mentioned that ionization potential is low and the hole injection from an anode plate is easy and that hole mobility is large. Until now for this purpose A porphyrin derivative and a phthalocyanine compound (JP,63–295695,A), Star bust mold aromatic series triamine (JP,4–308688,A), A hydrazone compound (JP,4–320483,A), the aromatic series diamine derivative of an alkoxy permutation (JP,4–220995,A), A p–(9–anthryl)–N and N–G p–tolyl aniline (JP,3–111485,A), Poly thienylene vinylene and Polly p–phenylenevinylene (JP,4–145192,A), Organic compounds, such as the poly aniline (refer to Appl.Phys.Lett., 64 volumes, 1245 pages, and 1994), Metallic oxides (the 43rd applied–physics relation union lecture meeting, 27 a–SY–1996 [9 or]), such as spatter carbon film (JP,8–31573,A), and a banazin san ghost, ruthenium oxide, a molybdic–acid ghost, are reported.

[0025] A porphyrin compound or a phthalocyanine compound is mentioned as a compound often used as the above-mentioned anode plate buffer layer ingredient. These compounds may have the central metal and the thing of a non-metal is sufficient as them. As an example of these desirable compounds, it is :porphin [to which the following compounds are mentioned] 5, 10, and 15, 20-tetrapod phenyl-21H, and 23H-porphin cobalt (II).

5, 10, 15, 20-tetrapod phenyl-21H, and 23H-porphin copper (II)

5, 10, 15, 20-tetrapod phenyl-21H, and 23H-porphin zinc (II)

5, 10, 15, and 20-tetra-phenyl-21 vanadium [H and 23H-porphin] (IV) oxide 5, 10, and 15, 20-tetrapod (4-pyridyl)-21H, 23H-porphin 29H, and 31H-phthalocyanine copper (II) phthalocyanine zinc (II) Phthalocyanine CHITANFUTAROSHIANIN oxide magnesium phthalocyanine lead phthalocyanine copper (II) 4, 4', 4", 4"'-tetraaza-29H, and 31H-phthalocyanine [0026] Although thin film formation is possible also for the case of an anode plate buffer layer like an electron hole transportation layer, in the case of an inorganic substance, a spatter, electron beam vacuum deposition, and a plasma-CVD method are used further. 3-100nm of thickness of the anode plate buffer layer 40 formed as mentioned above is usually 10-50nm preferably.

[0027] The electronic transportation layer 42 is formed on the electron hole transportation layer 41. An electronic transportation layer is formed from the compound which can convey the electron from cathode in the direction of an electron hole transportation layer efficiently in inter-electrode [which was able to give electric field]. As an electronic transportability compound used for the electronic transportation layer 42, the electron injection effectiveness from the up electrode (cathode) 23 is high, and it is required to be the compound which can convey the poured-in electron efficiently. For that purpose, to be the compound which the impurity which an electron affinity is large, and electron mobility is moreover large, is further excellent in stability, and serves as a trap cannot generate easily at the time of manufacture and use is demanded.

[0028] As an ingredient which fulfills such conditions, aromatic compounds, such as a tetra-phenyl butadiene (JP,57-51781,A), Metal complexes, such as an aluminum complex of 8-hydroxyquinoline (JP,59-194393,A), The metal complex of a 10-hydroxy benzo[h] quinoline (JP,6-322362,A), a mixed ligand aluminum chelate complex (JP,5-198377,A --) JP,5-198378,A, JP,5-214332,A, a JP,6-172751,A cyclopentadiene derivative (JP,2-289675,A), A peri non derivative (JP,2-289676,A), an OKISA diazole derivative (JP,2-216791,A), A bis-styryl benzene derivative (JP,1-245087,A, 2-222484 official report), A perylene derivative (JP,2-189890,A, 3-791 official report), A coumarin compound (JP,2-191694,A, 3-792 official report), A rare earth complex (JP,1-256584,A), a JISUCHIRIRU pyrazine derivative (JP,2-252793,A), p-phenylene compound (JP,3-33183,A), a thiadiazolo pyridine derivative (JP,3-37292,A),

A pyrrolo pyridine derivative (JP,3-3 and A), a NAFUCHI lysine derivative (JP,3-203982 silole derivative (03 or 70th spring annual convention [of the Chemical Society of Japan], 2D 1 02, and 2D1 19 etc. are mentioned. [0029] 10-200nm of thickness of the electronic transportation layer 42 is usually 30-100nm preferably. Although an electronic transportation layer can also be formed by the same approach as an electron hole transportation layer, a vacuum deposition method is usually used. Being the purpose which changes the luminescent color, while raising the luminous efficiency of a component, for example, doping fluorochromes for laser, such as a coumarin, by using the aluminum complex of 8-hydroxyquinoline as a host ingredient (J. Appl.Phys., 65 volumes, 3610 pages, 1989) etc. is performed. As for the advantage of this approach, usable and ** are mentioned also for an usable and 4 filmy fluorochrome with luminous efficiency bad [the fluorochrome from which luminescence wavelength starts adjustable and 3 concentration quenching by selection of improvement and two fluorochromes] by the fluorochrome of one well head.

[0030] Also in the purpose which improves the drive life of a component, it is effective to dope a fluorochrome by using said electronic transportation ingredient as a host ingredient. For example, the luminescence property, especially drive stability of a component can be greatly raised by doping condensed multi-ring aromatic series rings (JP,5-198377,A), such as a naphthacene derivative (JP,4-335087,A) represented by rubrene, the Quinacridone derivative (JP,5-70773,A), and perylene, 0.1 to 10% of the weight to a host ingredient by using metal complexes, such as an aluminum complex of 8-hydroxyquinoline, as a host ingredient.

[0031] As a host ingredient, when the electronic transportation layer 42 plays the role, the above-mentioned electronic transportability compound is mentioned, for example, and when the electron hole transportation layer 41 plays a role of a host ingredient, an above-mentioned aromatic amine compound and an above-mentioned hydrazone compound are mentioned. Although it is doped by homogeneity in the direction of thickness of each class when the above-mentioned dopant is doped in an electron hole transportation layer and/or an electronic transportation layer, there may be concentration distribution in the direction of thickness. For example, it may dope only near the interface with an electron hole transportation layer, or you may dope near the cathode interface conversely. [0032] In this invention, in order to attain full color luminescence, the following two approaches can be considered. One is the approach of making carry out white luminescence of the component, and decomposing the white light into three colors of blue, green, and red, using KARAFIRUTA as a luminescence conversion layer. Three colors of blue, green, and red are obtained by carrying out blue luminescence of the component, and blue's taking out the blue glow in a color as it is by using a fluorescence conversion layer as a luminescence conversion layer, and performing color conversion with a green fluorescence ingredient and a red fluorescence ingredient about green and red as another approach. Therefore, it is necessary to consider as the lamination in which white luminescence or blue luminescence is possible as an organic luminous layer. For this purpose, a luminescence function can be given to for example, an electronic transportation layer, and it can consider as the following lamination.

[0033] As shown in drawing 7, in white luminescence, the electronic transportation layer 42 can be divided into three fields 42a, 42b, and 42c, blue luminous layer 42a, green luminous layer 42b, red luminous layer 42c, then luminescence from each class can pile up and be put together from the direction which touches the electron hole transportation layer 41, and white luminescence can be obtained in it. In order to maintain white color balance, it can do easily by adjusting the thickness of each red luminous layer from blue. It can be used for the host ingredient and pan which are used for the electronic transportation layer mentioned already as an ingredient used for the luminous layer of each color combining dope coloring matter.

[0034] In blue luminescence, blue luminescence can be obtained in the already mentioned electronic transportation layer ingredient according to the host ingredient in which blue fluorescence is shown, and the structure shown in drawing 5 and drawing 6 by forming the electronic transportation layer which doped the blue fluorochrome if needed. As an approach of raising the luminous efficiency of organic electroluminescence devices further, the laminating of the electron injection layer 43 can also be further carried out on the electronic transportation layer 42 (refer to drawing 8). It is required for the compound used for this electron injection layer 43 that the electron injection from cathode should be easy and electronic transport capacity should be still larger. The aluminum complex of the 8-hydroxyquinoline already mentioned as an electronic transportation layer ingredient as such an electronic transportation ingredient, The system which distributed an OKISA diazole derivative (others [1989 / Appl.Phys.Lett., 55 volumes, 1489 pages, and]) and them to resin, such as a polymethyl methacrylate (PMMA), (Appl.Phys.Lett., 61 volumes, 2793 pages, 1992), phenanthroline derivative (JP,5-331459,A), 2-t-butyl -9, 10-N, and N'-dicyano anthraquinone diimine (Phys.Stat.Sol. (a) —) n mold hydrogenation amorphous carbonization silicon, n mold zinc sulfide, n mold zinc selenide, etc. will be mentioned in 142 volumes, 489 pages, and 1994. 5-200nm of thickness of an electron injection layer is usually 10-100nm preferably.

[0035] Since transparency is not required of <Approach B> lower electrode (cathode), the metal which usually fills the work function needed for electron injection is used. Although 4.0eV or less is desirable as a value of a work function, the metal which fulfills this value tends to oxidize, and if an oxide film generates on a front face, electron injection will become difficult in many cases. Moreover, in case patterning of the low work function metal is carried out using wet process, it is thought that neither scaling nor corrosion is avoided. Therefore, as for most parts, it is desirable to form with the metal of low resistance, for example, copper, aluminum, etc., using only the surface part of a lower electrode as a low work function ingredient layer. 2–100nm of thickness of this low work function ingredient layer is about 5–50nm preferably.

[0036] In this case, a low work function ingredient layer can be formed for example, by the vacuum deposition approach. As shown in <u>drawing 2</u>, the source and the drain electrode of TFT for an active drive are covered with

to prevent a short circuit with an up electrode the insulating protective coat 12 in insulating protective coat serves as wrap appearance completely except the part of a lower electrode. If a Th rt and this insulating protective coat are doubled, the distance from a lower electrode to the summit of an insulating protective coat will be set to about 3 micrometers. Since the thickness of a low work function ingredient layer is very thin as mentioned above and a level difference piece is easily raised at the wall edge in a vacuum deposition method, only the part on a lower electrode is connected electrically. Since the part formed on the insulating protective coat is in an insulating condition electrically, it does not carry out contribution of what to luminescence, either. [0037] The ingredient mentioned by Approach A is used as said low work function ingredient. Moreover, the volume phase shown by Approach A can be used instead of the above-mentioned low work function layer. It is Approach A and an ingredient and thickness are already described. Although a transparent electrode is required as an up electrode (anode plate), in order to pour in an electron hole efficiently, the ingredient which has a work function 4.6eV or more is desirable. For this purpose, a transparence oxide electrical conducting material like ITO or ZnO is used. Before forming the up electrode by transparence oxide electric conduction, metals with a more high work function (gold, palladium, etc.) may be formed in the translucent condition, and a component property may be raised.

[0038] Since it is the need that membranes are formed without raising a level difference piece also on the wall side face of the insulating protective coat described previously as the formation approach of an up electrode, the approach of forming membranes with sufficient covering power by whenever [low-vacuum] like a spatter is desirable. The laminating of the up transparence conductive layer is preferably carried out by about 10-500nm 5-1000nm of thickness. Moreover, solid membrane formation is sufficient over [electrode / up] the whole screen product.

[0039] About the structure of the organic luminous layer 9, it becomes the order of a laminating contrary to the lamination stated by Approach A. That is, in the configuration of drawing 5, it becomes the order of a substrate, a lower electrode, an electronic transportation layer, an electron hole transportation layer, and an up electrode. The same is said of the structure of drawing 6 and drawing 7. Finally, the transparence base material 24 with which the luminescence conversion layer 7 and it are formed is explained. In addition to taking out luminescence from an organic electroluminescence cel in support of a luminescence conversion layer, the role of a transparence base material has the function intercepted from the open air for closing a component. Although glass, a quartz, and the resin that carried out the coat of the suitable gas barrier layer are used for this purpose, when a glass plate takes into consideration cost, thermal resistance, and chemical resistance, generally it is desirable. [0040] About a luminescence conversion layer, two methods are in the appearance mentioned already. In combining with a white light emitting device, it forms a color filter on said transparence base material with a black matrix. There are not a color filter technique of existing [the formation approach] and a place which changes in any way. In the case of a fluorescence conversion layer, what distributed the fluorochrome to the resin medium instead of the pigment is used. It is also possible to give the function of a color filter to fluorescence conversion and coincidence. [0041] Although the transparence base material with which the insulating substrate which was produced as mentioned above, and which supports organic electroluminescence devices, and the luminescence conversion layer were formed is intercepted from the open air with a suitable spacer, heat curing, or photo-curing resin and the closure is carried out, it is desirable to use a thing with a size of 1-20 micrometers as a spacer in that case, and to

specify the distance between an insulating substrate and a transparence base material. In the distance of less than

luminescence conversion layer on a part for the light-emitting part which organic electroluminescence devices form

Imicro, damage may be done to a component in the case of handling, and a horizontal location gap of the

with an angle of visibility, and a transparence base material occurs in the distance of 20micro or more.



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EXAMPLE

[Example] Next, although an example explains this invention still more concretely, this invention is not limited to the publication of the following examples, unless the summary is exceeded. The example of manufacture of organic electroluminescence devices is shown below.

[0043] Example 1 (approach A)

According to Approach A, the component was produced in the process shown below. As a design of a TFT component, in the circuit diagram shown in <u>drawing 3</u>, gate length of the 1st TFT was made into 20 microns, gate width was made into 100 microns, gate length of the 2nd TFT was made into 20 microns, and gate width was made into 600 microns. Pixel area is 600 micron x600 micron, pixel spacing is 800 micron x800 micron, and the numerical aperture was made into 56%.

[0044] Each manufacture process is explained according to drawing 8 below.

(a) Patterning of the gate electrode which reaches what carried out the laminating of the Au by 20nm of thickness on aluminum film further what carried out vacuum deposition of the aluminum with the resistance heating method by 200nm of thickness lower electrode (anode plate) 22 with a usual photolithography technique and a usual wet etching technique on a lower electrode and a gate electrode formation process alkali-free-glass (7059 by Corning, Inc.) substrate was performed. It was 4.8eV when the work function of this lower electrode (anode plate) was measured by the Riken Keiki tabulation side analysis apparatus (AC-1).

[0045] (b) Gate dielectric film, the semi-conductor layer, and the substrate produced at the ohmic contact layer membrane formation process process (a) were set in plasma-CVD equipment, and continuation membrane formation of each class 3b, 4b, and 5b was carried out on the conditions shown in the following table -1.
[0046]

[Table 1]

- 表一 1

成膜条件	1.SiNx 届	2. i 雇 a-Si	3。n ⁺ 應a-Si
くガス流量>			
SiH4	10	20	10
NH3	100	_	_
H2	-	20	i –
PH3/H2 (0.1%)	_	-	100
恭板温度 [で]	300	280	280
成旗圧力 [Torr]	0.25	0.15	0.33
電力密度 [W/cm²]	0.14	0.08	0.08
護軍 [nm]	300	100 .	50

[0047] (c) Pick out a substrate from the plasma-CVD equipment of the a-Si patterning process above, and it is a usual photolithography technique and usual SF6. Plasma etching using gas performed patterning of a-Si. (d) By the source, and drain electrode formation process usual a photolithography technique and electron beam evaporation, the drain and source electrode which carried out the laminating of 50nm Cr layer and the 100nm aluminum layer one by one were formed.

[0048] (e) n+a-Si layer dirty off process usual a photolithography technique and SF6 By plasma etching using gas, the layer of n+a-Si was etched by having used the source and a drain electrode as the mask, and the channel was formed. When the property of a-SiTFT of the organic electroluminescence panel produced at the above-mentioned process (a) - the process (e) was evaluated, mobility (micro FE) was 0.5cm2 / V-sec, and the threshold was 3V. [0049] (f) The insulating layer of 1.3 micrometers of thickness was formed with the usual photolithography technique using the insulator layer formation process alkali development mold transparence heatproof resist ingredient for active-matrix circuit protection (the product made from Nippon Steel Chemistry; V-259PA).

After ultrasonic cleaning and pure water performed the drive circuit board done even at process (f) by isopropyl alcohol and rinsing and desiccation nitrogen performed desiccation, and UV / ozone washing, the adhesion mask which limits a vacuum evaporationo part was attached, and it installed in the vacuum evaporation system, and it exhausted using the oil diffusion pump until the degree of vacuum in equipment was set to 2x10 to 6 or less Torrs. [0050] The organic electroluminescence—devices part which has hereafter the white luminescence function of the structure shown in drawing 7 was produced. It vapor—deposited by heating the copper phthalocyanine (H1) (crystal form being beta mold) shown in the following put into the molybdenum boat arranged in the above—mentioned vacuum devices. It vapor—deposited with degree of vacuum 2x10-6Torr (about 2.7x10 to 4 Pa), and the evaporation rate of 0.3nm/second, and the anode plate buffer layer 40 of 20nm of thickness was obtained. [0051]

[Formula 1]

[0052] Next, it is the periphery [0053] of a crucible about the 4 and 4'-screw [N-(1-naphthyl)-N-phenylamino] biphenyl (H2) shown in the following put into the ceramic crucible arranged in said equipment. [Formula 2]

[0054] It vapor-deposited by heating at the tantalum wire heater of an enclosure. The temperature of the end crater which gets at this time was controlled in 250-260 degrees C. The electron hole transportation layer 41 of 60nm of thickness was obtained with degree of vacuum 1.7x10-6Torr at the time of vacuum evaporationo (about 2.3x10 to 4 Pa), and the evaporation rate of 0.3-0.5nm/second. The range of crucible temperature is 200-210 degrees C about the zinc OKISA diazole complex (E1) shown in the following structure expressions as an ingredient of electronic transportation layer 42a which has a blue luminescence function, and it is ** [0055].

[0056] It drove, and the degree of vacuum at the time of vacuum evaporation was 1.5x10-6Torr (about 2.0x10 to 4 Pa), the evaporation rate was 0.2-0.3nm/second, and the thickness of the vapor-deposited blue luminous layer was 30nm. Next, the 8-hydroxyquinoline complex (E2) of the aluminum shown below was similarly vapor-deposited as an ingredient which forms green luminous layer 42b. Controlling the end-crater temperature which gets at this time in 270-300 degrees C, the degree of vacuum at the time of vacuum evaporation carried out the laminating of 1.5x10-6Torr (about 2.0x10 to 4 Pa), and the evaporation rate on blue luminous layer 42a by 0.1-0.2nm /and 15nm of thickness a second.

[0057] 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)- which shows the 8-hydroxyquinoline complex (E2) of aluminum for red luminous layer 42c in the following structure expressions as dope coloring matter as a host ingredient as the last of a luminous layer — it used the 4H-pyran (DCM) (D1).

[0059] The range of the crucible temperature of the 8-hydroxyquinoline complex of the aluminum at this time is 270-300 degrees C, the crucible temperature of DCM was controlled in 100-110 degrees C, the degree of vacuum at the time of vacuum evaporationo is 1.3x10-6Torr (about 1.7x10 to 4 Pa), an evaporation rate is 0.1nm/second, and the laminating was carried out on green luminous layer 42c by 15nm of thickness. The amount which DCM contained in the 8-hydroxyquinoline complex of aluminum was 2 % of the weight. The substrate temperature when carrying out vacuum deposition of the above-mentioned anode plate buffer layer 40, the electron hole transportation layer 41, and each electronic transportation layers 42a-42c was held to the room temperature. [0060] (h) an up electrode formation process -- here, after exchanging the component which performed the vacuum evaporationo to the electronic transportation layer 42 for the shadow mask which specifies the vacuum evaporationo field and electrode takeoff connection of an up electrode, it was made to stick to a component, and it exhausted until it installed in another vacuum evaporation system and the degree of vacuum in equipment became below 2x10-6Torr (about 2.7x10 to 4 Pa) like the organic layer. Then, as cathode 4, the alloy electrode of magnesium and silver was vapor-deposited so that 2 yuan might become 20nm of thickness with coincidence vacuum deposition. Vacuum evaporationo was performed using the molybdenum boat in degree of vacuum 5x10-6Torr (about 6.7x10 to 4 Pa), and vacuum evaporationo time amount 3 minutes and 20 seconds. Moreover, the atomic ratio of magnesium and silver was set to 10:1.4. The work function of the Magnesium alloy of this presentation was 3.6eV. Then, the component was moved to the sputtering system, the laminating of the ITO film was carried out on magnesium and the silver alloy film by 150nm thickness, and the up electrode 23 was completed. By the usual RF magnetron sputtering method, the component performed the spatter, without heating. As spatter conditions for ITO, the mixed gas (0.1% of oxygen densities) of argon-oxygen, pressure 3x10-3Torr (about 0.4Pa), power-flux-density 0.1 W/cm2, a target, and distance between substrates were set to 10cm, in order to prevent a plasma damage. The work function of the ITO film obtained as mentioned above was 4.7eV. [0061] (i) It is a target within the still more nearly same sputtering system on the component which even the protective coat formation process up electrode formed SiO2 It carries out and is transparent SiO2. The protective

coat was formed by 1000nm of thickness.

(j) The component ended to the closure process process (i) was taken out in the box permuted with dry nitrogen, TFT and the organic luminescence cel substrate which applied the photo-setting resin to the periphery for the glass substrate which carried out patterning of the color filter (blue, green, red) so that it might be in agreement with the electrode pattern of an organic electroluminescence cel as a luminescence conversion layer beforehand, and after the marker performed alignment, UV exposure was carried out and hardening processing was completed. At this time, the distance of an organic luminescence cel substrate and a color filter substrate was set up with 5 micrometers by making photo-curing resin distribute a silica bead with a diameter of 5 micrometers. The color filter was formed using the color resist according to the approach usually learned, the transparence smoothing layer was

[0062] When the organic electroluminescence devices completed at the above-mentioned process were made to drive, luminescence of green [which were changed in each color filter layer / the red and green], and blue has been checked. Moreover, the full color image has been attained by carrying out gradation control of blue, green, and the luminescence brightness of each red subpixel.

Example 2 (approach B)

According to Approach B, the component was produced in the process shown below. The design of a TFT component is the same as an example 1. Each manufacture process is explained according to <u>drawing 8</u> below. (a') A usual photolithography technique and a usual wet etching technique performed patterning of the lower electrode (cathode) 22 and a gate electrode for what formed Cr for aluminum by the sputtering method by 50nm of thickness further 200nm of thickness on the lower electrode and the gate electrode formation process alkali—free-glass (7059 by Corning, Inc.) substrate.

[0063] A process (b) – a process (f) are performed like an example 1.

prepared on it, and all thickness could be 3 micrometers.

(g') Organic electroluminescence layer membrane formation process (blue luminescence cel)

Then, the low work function layer of a lower electrode (cathode) was formed by the following approaches. After ultrasonic cleaning and pure water performed the drive circuit board done even at the process (f) by isopropyl alcohol and rinsing and desiccation nitrogen performed desiccation, and UV / ozone washing, the shadow mask which specifies a vacuum evaporation field and an electrode takeoff connection was stuck for the component, and it exhausted until it installed in the vacuum evaporation system and the degree of vacuum in equipment became below 2x10-6Torr (about 2.7x10 to 4 Pa) like the organic layer. As a low work function layer of a lower electrode, the alloy electrode of magnesium and silver was vapor—deposited so that 2 yuan might become 50nm of thickness with coincidence vacuum deposition. The work function of this Magnesium alloy was 3.6eV.

[0064] The organic electroluminesce devices part which has hereafter the white lume ence function of the structure shown in drawing 8 was produced. The anode plate buffer layers 40 and 4 of 2 of thickness which consists of a copper phthalocyanine (H1), and the electron hole transportation layer 41 of 60nm of thickness which consists of a 4'-screw [N-(1-naphthyl)-N-phenylamino] biphenyl (H2) were formed like the making process of an example 1. Next, the aluminum 2 angle complex (E1) of the 2-methyl-8-hydroxyquinoline shown in the following structure expressions as a host ingredient of the electronic transportation layer 42 which has a blue luminescence function and [0065]
[Formula 5]

[0066] About the perylene (D2) shown in the following structure expressions as dope coloring matter, it is a separate crucible [0067] respectively.

[0068] ******* vacuum evaporationo of 2 yuan was performed. The range of the crucible temperature of the aluminum 2 nucleus complex at this time is 300-320 degrees C, the crucible temperature of perylene was controlled in 110-120 degrees C, the degree of vacuum at the time of vacuum evaporationo is 1.8x10-6Torr (about 2.4x10 to 4 Pa), an evaporation rate is 0.2-0.3nm/second, and the laminating of the blue luminous layer of 45nm of thickness was carried out on the electron hole transportation layer 41.

[0069] Finally, the 8-hydroxyquinoline complex (E2) of aluminum was used as an electron injection layer. The crucible temperature of the 8-hydroxyquinoline complex of the aluminum at this time was controlled in 270-280 degrees C, the degree of vacuum at the time of vacuum evaporation is 1.3×10 -6Torr (about 1.7×10 to 4 Pa), an evaporation rate is 0.2-0.3nm/second, and the laminating of the electron injection layer of 30nm of thickness was carried out on the electronic transportation layer. The substrate temperature when carrying out vacuum deposition of the anode plate buffer layer 40, the electron hole transportation layer 41, the above-mentioned electronic transportation layer 42, and the above-mentioned electron injection layer 43 was held to the room temperature. [0070] (h') The ITO film was formed by 150nm thickness as an up electrode formation process, then an up electrode (anode plate). By the usual RF magnetron sputtering method, the component performed the spatter, without heating. As spatter conditions for ITO, the mixed gas (0.1% of oxygen densities) of argon-oxygen, pressure 3×10 -3Torr (about 0.4Pa), power-flux-density 0.1 W/cm2, a target, and distance between substrates were set to 10cm, in order to prevent a plasma damage. The work function of this anode plate was 4.7eV.

[0071] Then, after passing through a protective coat formation process (i), the fluorescence conversion layer was used as a luminescence conversion layer, and also the closure process (j) as well as an example 1 was performed, and the stroke was made to complete like Approach A. Since blue luminescence was used as it was as a fluorescence conversion layer, it was unnecessary, and after distributing a coumarin 6 and distributing phenoxazone 660 for the thing which made PMMA distribute a coumarin 6 3% of the weight about a green fluorescence conversion layer 2% of the weight in PMMA 1% of the weight as a red fluorescence conversion layer, the laminating of the transparence smoothing layer was carried out, and it formed by 3 micrometers of all thickness.

[0072] When the organic electroluminescence devices completed at the above-mentioned process were made to drive, luminescence of the clear red changed in each fluorescence conversion layer, green, and blue has been checked.



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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[<u>Drawing 1</u>] The type section Fig. having shown an example of the conventional organic electroluminescence devices.

[Drawing 2] The type section Fig. having shown an example of the organic electroluminescence devices used for this invention.

[Drawing 3] The example of a circuit for the drive of the organic electroluminescence devices of this invention.

[Drawing 4] The TFT drive circuit top view of the organic electroluminescence devices of this invention.

[Drawing 5] The type section Fig. having shown an example of an organic electroluminescence cel.

[Drawing 6] The type section Fig. having shown another example of an organic electroluminescence cel.

<u>[Drawing 7]</u> The type section Fig. having shown another example of an organic electroluminescence cel.

[Drawing 8] The type section Fig. having shown another example of an organic electroluminescence cel.

[Drawing 9] The example of a making process of the organic electroluminescence panel of this invention.

[Drawing 10] The example of a making process of the organic electroluminescence panel of this invention.

[Description of Notations]

1 Transparence Substrate

2 Gate Electrode of TFT

3 Gate Dielectric Film

4 Semi-conductor Laver

5 Ohmic Contact Layer

6a, 6b A source electrode, drain electrode

7 Luminescence Conversion Layer

8 Anode Plate

9 Organic Luminous Layer

10 Cathode

11 Tooth-Back Plate

21 Insulating Substrate

22 Lower Electrode (Anode Plate or Cathode)

23 Up Electrode (Cathode or Anode Plate)

24 Transparence Base Material

31,32 TFT1,TFT2

33 Capacitor for Are Recording

34 Scanning Line

35 Data Line

36 Common Line

37 Pixel Lower Electrode

38 Gate Dielectric Film / Semi-conductor Layer

40 Anode Plate Buffer Laver

41 Electron Hole Transportation Layer

42, 42a-42c Electronic transportation layer

43 Electron Injection Layer

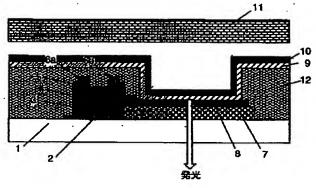


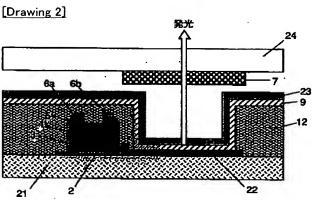
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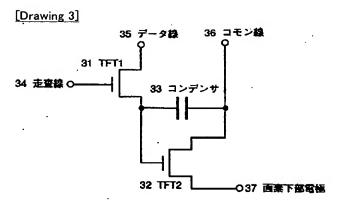
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DRAWINGS

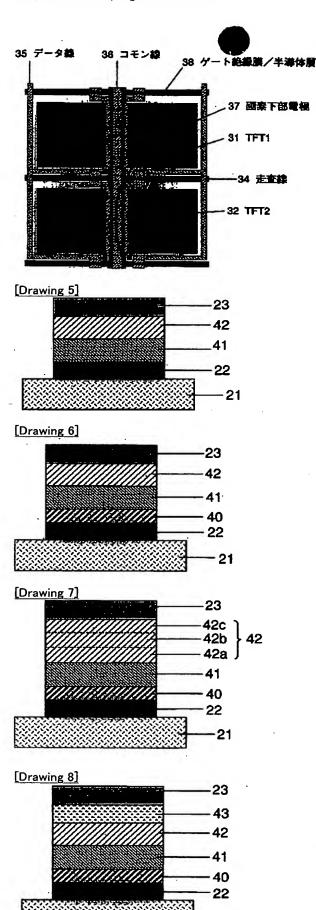
[Drawing 1]



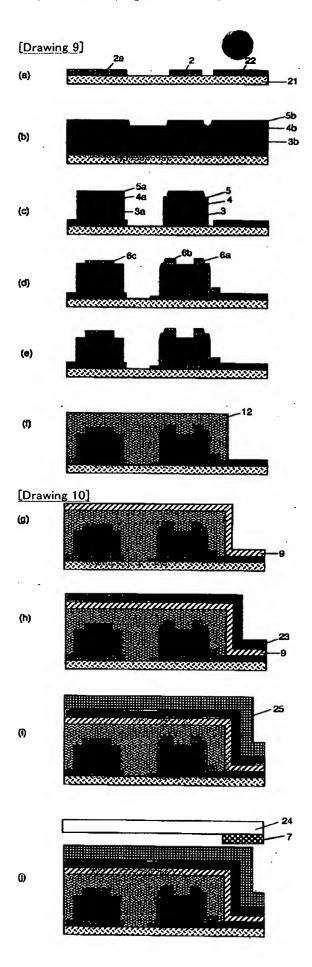




[Drawing 4]



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